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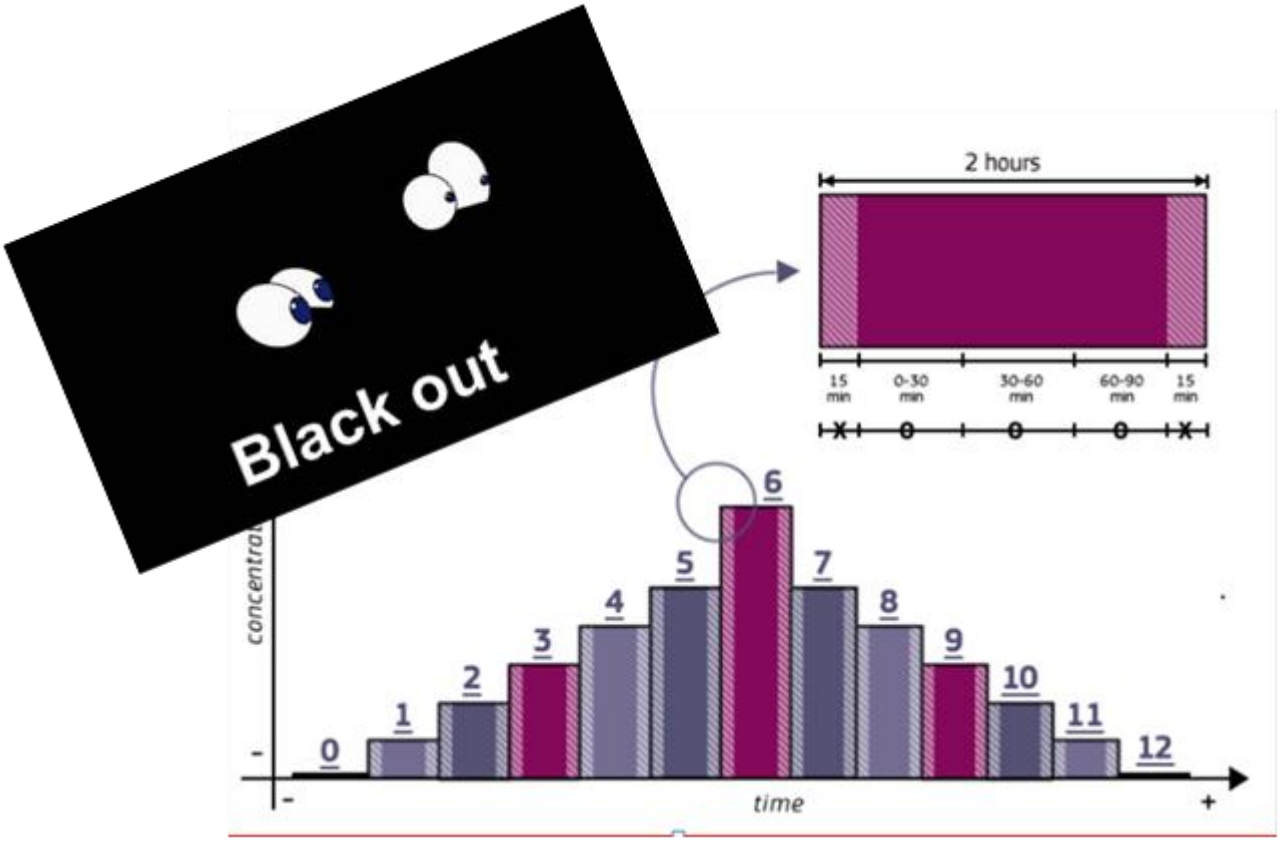

Third EC-JRC aromatic compounds inter-laboratory comparison with automatic analysers

Ispra, November 2013

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Abstract

This report presents the results of the third inter-laboratory comparison for BTEX automatic analysers performed at the JRC on the 12-15 November 2013. Nine national reference laboratories with a total of eleven instruments, participated in this exercise. Six concentration levels were tested during the inter-laboratory comparison. Benzene concentrations ranged from 1 to 50 µg/m3. The exercise was evaluated according to ISO 13528 methodologies for the evaluation of inter-laboratory proficiency assessment and the recommendation of the protocol N37 of the AQUILA network. Participating laboratories are identified as requested by the AQUILA protocol.
The report compares reference and robust average values for the three up and down concentration series tested during the exercise, gives information on the technique and instrumentation used by each participant and shows the linearity test, identification of outliers, repeatability, reproducibility and robustness of the methodology, as well as parameters to evaluate laboratory results: repeatability score, bias and En values.
In spite of an unforeseen power failure occurred during the comparison, which lead to a shutdown of all instruments and gas generation for three hours, the comparison exercise could be resumed successfully. The results show a substantial improvement with respect to the previous two inter-laboratory exercises with robust values for the benzene measurements that were in line with average reproducibility values of 7.8 %..

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Executive Summary

This report presents the results of the third inter-laboratory comparison for BTEX automatic analysers performed at the JRC on the 12-15 November 2013. Nine national reference laboratories with a total of eleven instruments, participated in this exercise. Six concentration levels were tested during the inter-laboratory comparison. Benzene concentrations ranged from 1 to 50 µg/m^3. The exercise was evaluated according to ISO 13528 methodologies for the evaluation of inter-laboratory proficiency assessment and the recommendation of the protocol N37 of the AQUILA network. Participating laboratories are identified as requested by the AQUILA protocol.

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In spite of an unforeseen power failure occurred during the comparison, which lead to a shutdown of all instruments and gas generation for three hours, the comparison exercise could be resumed successfully. The results show a substantial improvement with respect to the previous two inter-laboratory exercises with robust values for the benzene measurements that were in line with average reproducibility values of 7.8 %.

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Nomenclature and abbreviations

AAA: Environmental Protection Agency (Lithuania)

AEA: Ricardo AEA (United Kingdom)

AQUILA: air quality reference laboratories

BTEX: benzene, toluene, ethyl-benzene, xylene

CG: gas chromatograph

D.D.: Dynamic Dilution

EEA; Executive Environment Agency

EC: European Commission

EKONERG: Energy and Environmental Protection Institute (Croatzia)

EPA: Environmental Protection Agency (Ireland)

ERLAP: European Reference Laboratory of Air Pollution

EU: European Union

FID: flame ionization detector

GIOS: Chief Inspectorate of Environmental Protection (Poland)

H.C.: hydrocarbons

HMS: Air Quality Reference Centre, Hungarian Meteorological Service (Hungary)

ISCIII: Instituto de Salud Carlos III (Spain)

ISO: International Standard Organisation

IHP_S: Institute of Public Health (Serbia)

LV: limit value

QAQC: quality assurance quality control

n.a.: not available

NPL: National Physical Laboratory (United Kingdom)

NRL: National Reference Laboratory

PID: photo ionization detector

ppb (m/m): part per billion, molar fraction

Press. Cyl.: presssurised cylinder

Tr. Std.: travelling standard

$\overline{C_i}$: average concentration value of i measurements

$\overline{\overline{C}}$: inter-laboratory average concentration

$\overline{C_i}^*$: robust average value

C_{ref}: reference concentration value

$$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$$

k_i: Mendel-k value for laboratory i

n: number of replicated analysis

p: number of participating laboratories

P(Z): probability function of the random variable Z.

R_c: residuals of the linear regression $\overline{C}_i$ vs C_{ref} at the evaluated concentration level, C

s^*: standard deviation of the robust average value $\overline{C}_i^*$

s_{bias} : standard deviation of the bias, $\overline{C}_i^* - C_{ref}$

$S_{\bar{c}_i}$: standard deviation of the average inter-laboratory value

s_i: standard deviation of the sample i.

s_L^2: inter-laboratory variance or between-laboratory variance

$s_{L_{N37}} = \sqrt{\hat{\sigma}_{N37}^2 - \frac{s_r^2}{n}}$: between laboratory standard deviation from the prescript conditions of proficiency assessment of AQUILA network.

s_r^2: repeatability variance or intra-laboratory variance

s_R^2: reproducibility variance

u: uncertainty of the method

u_{Cref}: uncertainty associated with the reference concentration value C_{ref}

$\mu g/m^3$: micrograms per cubic meter

α: level of significance

$\gamma = s_R/s_r$: gamma value

σ: standard deviation

$\hat{\sigma}$: standard deviation for proficiency assessment

$\hat{\sigma}_m = \sqrt{(0.5 \cdot s_L)^2 + \frac{s_r^2}{n}}$: minimum standard deviation of proficiency assessment coherent with method reproducibility

$\hat{\sigma}_{N37}$: standard deviation for proficiency assessment prescript by AQUILA network

(1-α): confidence level

Introduction

In accordance with the EC directive 2008/50/EC and following on from the two previous EC-JRC aromatic BTEX inter-laboratory comparisons for automatic analysers [EUR 22523 EN and EUR23792EN], this inter-laboratory comparison exercise was framed in the QAQC programme for the harmonization of air quality measurements in Europe and, in particular, for benzene.

This exercise aims to evaluate capacity of the participating laboratories to quantify the analyte of interest over a pre-defined range of concentrations. As a difference from the two previous exercises, laboratories were asked to report the average value determined for each concentration level and the corresponding associated uncertainty. Individual results were evaluated according to the repeatability-score and the E_n value. As agreed within AQUILA protocol participating laboratories have been identified in the report.

Inter-laboratory comparison strategy

The inter-laboratory comparison was carried out at the JRC Ispra site bench facilities from 12th to 15th November 2014. Registration of the participants including description of the instrumentation that would be used during the exercise closed on the 15th May 2013.

The reporting of data results from the participating laboratories was carried out by uploading the requested information on the JRC web site application at http://interlabo-comparison.jrc.ec.europa.eu. This included: characteristics of the BTEX analyser, description of the calibration method and traceable reference material, average concentrations and corresponding analytical uncertainties for each concentration step. Reported information from the participants is collected in the annex.

The exercise was initially programmed for a zero air check and an up and down six-step concentration levels of two hours each one (L series). This was to allow the different automatic analysers to perform three or six complete measurements of 30 or 15 minutes, respectively. Unfortunately, a few hours after the start of the exercise a general black-out affected all running instrumentation and test gas generation. The three hour electricity power interruption mainly affected the measurements of the first sequence in course by losing all the data from the third step of increasing concentration of the series. Although most of the instruments were able to re-start automatically when the electricity came back, the exercise was re-initiated the following day to ensure the testing of the instrumentation along the full range of concentration within the remaining time of the exercise. Two consecutive series of up and down six-step concentrations (S1 and S2 series) were launched with a shorter time, one hour, in each concentration step, but

allowing a complete 30 minutes measurement or two of 15 minutes, depending on the instrument. The final time schedule of the exercise is given in the annex.

In this exercise concentrations were expressed in µg/m^3 at 20 °C and 1 atm. Conversion factors from ppb (v/v) to µg/m^3 for reporting results were agreed before comparison (see annex).

Participating laboratories and instrumentation

Nine NRLs participated in the inter-laboratory comparison exercise. Table 1 shows the name of the participating laboratories. VMM and EPA reported results from two different instruments.

Table 2 identifies the type of instrumentation used by each laboratory. From the eleven instruments that were involved in this exercise only three instruments used flame ionization detector (FID), while the rest of the instruments used a photo ionization detector (PID). Table 3 shows the reference material or travelling standard used by each laboratory to calibrate their analysers.

Table 1.- List of participating laboratories

Acronym	Laboratory	Country	Contact
VMM	Vlaamse milieumaatschappij	Belgium	Jan Petré, David Roet, Vincent Keppens
EKONERG	Energy and Environmental Protection Institute	Croatia	Predag Hercog, Marijo Bilic
HMS	Air Quality Reference Centre, Hungarian Meteorological Service	Hungary	Viktor Dézsi, Attila Machon
EPA	Environmental Protection Agency	Ireland	Lin Delaney, Barbara O'leary
AAA	Environmental Protection Agency	Lithuania	Juozas. Molis, Aurelijus Jurkus
GIOS	Chief Inspectorate of Enviromental Protection	Poland	Tomasz Frackowski, Andrzej Pindel
IHP_S	Institute of Public Health	Serbia	Andrej Sostaric, Ljiljana Adjanski
ISCIII	Instituto de Salud Carlos III	Spain	Rosalia Fernandez Patier, Pilar Morillo , Ogura Mogura

AEA	Ricardo AEA	United Kingdom	James Dernie, Michael Davies Peter Dumitrean, Steve Telling, Brian Stacey,

Table 2.- Instrumentation used by the participants during the inter-laboratory comparison exercise

Code	Analyser	Cycle time, min	Detector	Column: Length, i.d.*, film tickness Operational conditions	Adsorbent Desorption conditions
VMM1	Airmotec BTX HC 1000, gC866, 1011	15	FID	**MXT30CE:** 30 m, 0.28 mm, 1 µm 43°C,2°C/min, 45°C,10°C/min, 75°C,15°C/min, 165°C,(120')	**Carbotrap-B** 380°C for 120 s, 3-4 ml/min
VMM2	SYNSPEC Analyser GC 955, 2006	15	PID	**AT-624:** 13 m, 0.32 mm, 1 µm 50°C (3'),2°C/min,70°C (7')	**Tenax GR** 180°C for 54 s, 1.5 ml/min
EKONERG	Chromatorec Airmo BTX 1000, 2011	15	FID	**MXT30CE:** 30 m, 0.28 mm, 1 µm 60°C,15°C/min,165°C)	**Carbotrap-B** 380°C for 120 s, 4 ml/min
HMS	CHROMATOTEC AIRMOTEC, AIRMO VOC C6-C12, A3100, 2003	30	FID	**MXT30CE:** 30 m, 0.28 mm, 1 µm 36°C,2°C/min, 38°C,2°C/min, 50°C,10°C/min, 80°C,15°C/min, 200°C'	**Carbotrap-B** 380°C for 240 s, 3 ml/min
EPA1	SYNTECH Analyser GC 955, Vers. 600, 2008	15	PID	**CP-Sil8 CB**, 13 m, 0.32 mm, 1µm 50°C (180 s),10°C/min, 50°C (7'), 10°C/min ,50°C	**Tenax GR 35/60** 180°C for 60 s, 1.5 ml/min
EPA2	SYNTECH Analyser GC 955, Vers. 611, 2010	15	PID	**CP-Sil8 CB**, 13 m, 0.32 mm, 1µm 50°C (180 s),10°C/min, 50°C (7'), 10°C/min ,50°C	**Tenax GR 35/60** 180°C for 60 s, 1.5 ml/min
AAA	AMA Instrument, CG5000 BTX FID, VERS 3, 2011	30	FID	**AMAsep1,** 30 m, 0.32 mm, 1.5 µm 50°C (180 s),8°C/min,130°C (5')	**Carbotrap** 230°C for 180 s, 2 ml/min
GIOS	SYNTECH SPECTRAS GC 955, 2011	15	PID	**SY-5:** 13 m, 0.32 mm, 1 µm 50°C (1-3'),10 °C/min,70°C (5-12'), -8 °C/min,50°C (13.5-15')	**Tenax GR** 180°C for 26 s, 1.5 ml/min
IPH_S	SYNTECH SPECTRAS Analyser GC 955, 2009	15	PID	**AT-624:** 13 m, 0.32 mm, 1 µm 50°C (3'),10°C/min,70°C (6') - 10°C/min 50°C	**Tenax GR** 180°C for 60 s, 1.5 ml/min
Carlos III	SYNTECH SPECTRAS Analyser GC 955, 2004	15	PID	**AT-624:** 13 m, 0.32 mm, 1.8 µm 50°C (3'),10°C/min,70°C (6') - 10°C/min 50°C	**Tenax GR** 180°C for 40 s, 1.5 ml/min
AEA	Environnement SA.VOC 71M	15	PID	**SPB-624:** 13 m, 0.32 mm, 1.8 µm 34°C (115 s),20°C/min,150°C (155 s)	**Carbotrap/Carbopak-X** 350°C for 180 s, 1 ml/min

Table 3.- Reference material used by the participating laboratories

Laboratory	Reference Material	Benzene ppb(m/m)*	Toluene ppb(m/m)*	Ethyl-benzene ppb(m/m)*	m-Xylene ppb(m/m)*	p-Xylene ppb(m/m)*	o-Xylene ppb(m/m)*	Other compounds	Producer	Certified by	Certification date
VMM	P.T **D.D**.	11.33± 0.84 ng/min	10.64±0.95 ng/min	6.42 ± 0.75 ng/min	8.63 ± 0.95 ng/min	8.63 ±0.95 ng/min	17.34 ±1.42 ng/min	-	GRACE	GRACE	16/01/2013
EKONERG	Press. Cyl.	12 ± 0.36	11.96±0.36	12.05 ± 0.36	11.88±0.36	12.03±0.36	11.71±0.36	_	VSL	VSL	n.a.
HMS	Press. Cyl. **D.D**. Environics 200	986±29	985±29	995±29	983±29	982±29	1014±29	-	VSL	VSL	21/10/2013
EPA	Press. Cyl.	10.14±0.20	10.27±0.26	0.69 ± 0.24	10.18±0.25	9.80± 0.25	10.25± 0.26	-.	NPL	NPL	23/09/2013
AAA	Press. Cyl. **D.D.** Dilutor:Um.MCZ	4990±100	5110±100	-	-	-	-	-	NPL	NPL	n.a.
GIOS	Press Cyl **D.D.**	1117±55.85	855±8.5	815±8.15	714±7.14	695±6.95	650±6.50		Air Liquid	Air Liquid	10/10/2013
IHP_S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.
ISCIII	Press. Cyl. **D.D.** (API model 700)	149.9 ± 4.5	149.3 ± 4.5	150.5 ± 4.5	148.1 ± 4.5	150.3± 4.5	146.2 ± 4.5	_	VSL	VSL	22/08/2012
AEA	Press. Cyl.	3.76 ± 0.08	3.78 ± 0.08	3.81 ± 0.08	3.78 ± 0.08	3.80± 0.08	3.80 ± 0.08	30 H.C. mixture.	NPL	NPL	n.a.

Press. Cyl.: Pressurised cylinder; D.D.: Dynamic Dilution; H.C.: Hydrocarbons; n.a.: not available; P.T.: Permeation Tubes

**: ppb(m/m): concentration in part per billion with respect to molar fraction ± its expanded uncertainty (k=2)*

Reference values

Two instruments (a BTEX Chrompack mod. 7001 and a GC Agilent 7890A coupled with an on-line sampling Thermal Desorber Unity from Markes) were used by ERLAP to trace the concentrations during the exercise. These instruments were calibrated against reference material (NPL Primary reference gas mixture: Reference 2013060383) by a multipoint calibration over the operative concentration range of the exercise. Nevertheless, due to the unforeseen power interruption and the memory effect on the operating instrumentation, final reference values were adopted from those determined by the dilution of the standard cylinders used during the exercise. In this case, flows and concentrations were traceable to primary and gravimetric international standards. Uncertainties for the reference concentrations were, however, estimated on the basis of the biases calculated with respect to the value measured by ERLAP.

Reference concentrations and calculated uncertainties for each level of concentration are given in table 4.

Table 4.- Reference values and associated uncertainties of the exercise

	Benzene					Toluene				
Level	**L**	**L**	**S1 & S2**	**S1**	**S2**	**L**	**L**	**S1 & S2**	**S1**	**S2**
	Conc., µg/m^3	**Unc,**.1σ %	**Conc.,** µg/m^3	**unc.,** 1σ %	**unc.,** 1σ %	**Conc.,** µg/m^3	**unc.**, 1σ %	**Conc.,** µg/m^3	**unc.,** 1σ %	**unc.**,1σ %
1ST-A	1.29	6.25	1.04	13.37	10.11	4.74	7.23	3.84	10.05	6.12
2ND-A	3.00	1.14	3.10	0.34	0.50	10.54	4.50	10.85	0.11	1.96
3RD-A	5.03	2.31	5.17	1.90	1.78	17.67	2.97	18.09	1.56	1.65
4TH-A	10.15	2.10	10.41	1.05	0.30	35.62	2.36	36.45	1.21	0.94
5TH-A	30.43	0.83	31.23	1.06	1.02	106.81	1.54	109.33	0.32	0.26
6TH-A	49.65	2.78	52.05	0.20	0.33	175.64	2.83	182.94	0.39	0.32
5TH-B	30.28	1.26	31.23	0.06	0.37	106.29	2.06	109.33	0.86	0.62
4TH-B	10.12	2.29	10.41	1.24	1.32	35.54	2.97	36.45	1.90	1.75
3RTD-B	5.01	2.62	5.17	2.23	3.06	17.57	3.28	18.09	2.42	2.44
2ND-B			3.10	4.28	4.40			10.85	3.36	3.33
1ST-B			1.04	13.81	15.10			3.84	11.83	12.40

	Ethyl benzene					m,p-Xylene				
Level	**L**	**L**	**S1 & S2**	**S1**	**S2**	**L**	**L**	**S1 & S2**	**S1**	**S2**
	Conc., µg/m^3	**Unc,**.1σ %	**Conc.,** µg/m^3	**unc.,** 1σ %	**unc.,** 1σ %	**Conc.,** µg/m^3	**unc.**, 1σ %	**Conc.,** µg/m^3	**unc.,** 1σ %	**unc.**,1σ %
1ST-A	0.92	7.38	0.56	39.68	26.47	0.92	18.02	0.63	79.40	56.77
2ND-A	2.01	2.90	2.02	1.33	2.37	2.02	24.78	2.11	2.71	9.04
3RD-A	3.38	2.00	3.37	4.31	3.98	3.39	3.03	3.52	8.03	7.03
4TH-A	6.80	0.98	6.79	2.62	2.05	6.84	1.61	7.09	3.62	2.76
5TH-A	20.40	0.64	20.37	0.56	0.50	20.51	1.44	21.28	0.34	0.50
6TH-A	33.42	2.52	33.80	1.72	1.44	33.43	3.61	35.42	0.21	0.05
5TH-B	20.30	1.25	20.37	1.87	1.40	20.41	2.04	21.28	0.91	0.77
4TH-B	6.79	1.91	6.79	3.62	3.14	6.82	2.75	7.09	4.63	4.16
3RTD-B	3.36	2.31	3.37	5.24	5.41	3.37	3.34	3.52	9.01	9.13
2ND-B			2.02	8.03	7.81			2.11	15.93	15.57
1ST-B			0.56	33.94	36.32			0.63	64.35	67.95

	o-Xylene				
Level	**L**	**L**	**S1 & S2**	**S1**	**S2**
	Conc., µg/m^3	**Unc,**.1σ %	**Conc.,** µg/m^3	**unc.,** 1σ %	**unc.**, 1σ %
1ST-A	0.55	44.12	0.69	41.27	32.05
2ND-A	2.04	10.51	2.21	2.38	2.53
3RD-A	3.41	5.77	3.69	6.05	4.69
4TH-A	6.88	4.01	7.44	2.41	1.68
5TH-A	20.62	3.59	22.31	0.07	0.01
6TH-A	32.74	6.85	37.71	0.18	0.50
5TH-B	20.52	4.18	22.31	1.32	0.88
4TH-B	6.86	5.09	7.44	3.33	2.90
3RTD-B	3.39	6.09	3.69	5.89	5.43
2ND-B			2.21	9.29	9.33
1ST-B			0.69	41.24	41.80

Statistical considerations

Linearity test

Linearity of the analysers was tested according to EN14662-3 by comparing the average value of the reported results at each level and instrument, $\overline{C}_i$, with its respective reference value, C_{ref}, at this level. Residual, R_c, is calculated according to the following expression:

$$R_c = \overline{C}_i - (a + b \cdot C_{ref}) \qquad \textbf{Eq. 1}$$

where *a* and *b* are the correlation coefficients of the corresponding linear regression ($\overline{C}_i$ vs C_{ref}). As a criterion of linearity, the maximum accepted value as residual is 5%.

Repeatability, reproducibility and robustness of the method

The repeatability and reproducibility derived from the inter-laboratory comparison exercise results were calculated after the elimination of outliers identified by Mandel's h and k statistic:

The ***inter-laboratory consistency*** is determined by the statistic ***h***, which represents the ratio between the bias of the measure with respect to the average value, $\overline{C_i}$, and the standard deviation of the average inter-laboratory values, $S_{\bar{C}_i}$.

The ***intra-laboratory consistency*** is determined by the statistic ***k***, which is defined by the ratio between the laboratory standard deviation of the sample, $\mathbf{s_i}$, and the pooled within-laboratory standard deviations:

$$k_i = \frac{s_i}{\sqrt{\frac{\sum s_i^2}{p}}} \qquad \textbf{Eq. 2}$$

Indicators for Mandel's statistics at the 1 and 5 % level of significance are given in the annex. These values determine the outliers and stragglers, respectively.

As a result, the uncertainty of the inter-laboratory average value, $\overline{\overline{C}}$, is determined by the combination of the inter-laboratory variance, s_L^2, and the intra-laboratory variance (repeatability variance), s_r^2. The addition of both variances represents the reproducibility variance, s_R^2, in this case being the variance associated with the uncertainty of the method [ISO 5725 Part 1, Part 2, 1994]:

$$u = \sqrt{s_L^2 + s_r^2} = s_R \qquad \textbf{Eq. 3}$$

being

$$s_r^2 = \frac{1}{p}\sum_i^p s_i^2$$

$$s_R^2 = \frac{1}{p-1}\sum_i^p \left(\overline{C}_i - \overline{\overline{C}}\right)^2 + \left(1 - \frac{1}{n}\right)\cdot s_r^2 \qquad \textbf{Eq. 4, Eq. 5}$$

where 'p' is the number of laboratories; 'n' is the number of replicated analyses done by each laboratory; 's_i' and '$\overline{C_i}$' are the standard deviation and average value corresponding to the laboratory 'i'.

The null hypothesis for equivalence between the inter-laboratory averages can be used as a criterion for the robustness of the method tested. Such an hypothesis assumes a F-distribution with *p-1* and *p(n-1)* degrees of freedom for the statistic F defined by the ratio: s_L^2 / s_r^2 This unilateral test for the F-distribution statistic depends on the degrees of freedom (experimental design: number of participating laboratories and replicated samples) and the accepted significance level. As a conservative approach, methods with F-values lower than 3 can be considered as robust methods. This criterion expressed as a ratio between reproducibility and repeatability standard deviations implies gamma values, γ, lower than 2, being $\gamma = s_R/s_r$ [P. Pérez Ballesta et al., 2001].

Repeatability score

Following the AQUILA N37 recommendations, the standard deviation for the proficiency assessment, $\hat{\sigma}_{N37}$ is calculated as a function of the concentration level in μg/m^3, C, by the following equation:

$$\hat{\sigma}_{N37} = 0.128 + 0.057 \cdot C \qquad \textbf{Eq. 6}$$

A repeatability score has been derived from the k-statistic in order to evaluate the performance criterion as established by EN 14662-3 for benzene automatic analysers, i.e. 5 % at the limit value and 0.3 % for values lower than 0.1 x LV. In this case the pooled-within-laboratory standard deviation is replaced by the corresponding maximum accepted repeatability value or, alternatively by the associated uncertainty of the reference value, when this value is limiting the repeatability

test. Repeatability scores values lower than $\sqrt{2}$ are considered acceptable, between $\sqrt{2}$ and $\sqrt{3}$ are questionable and higher than $\sqrt{3}$, i.e. outside the 99 % confidence level, are considered as poor performer.

Minimum standard deviation of the proficiency assessment

In agreement with ISO 13528, the ratio between the between-laboratory standard deviation of the inter-laboratory comparison, s_L, and that derived from the prescribed standard deviation for the proficiency assessment, s_{LN37}, should be lower than 2 to represent a realistic choice. So, as the between-laboratory standard deviation from prescript conditions of proficiency assessment is calculated according to the following expression:

$$s_{L_{N37}} = \sqrt{\hat{\sigma}_{N37}^2 - \frac{s_r^2}{n}} \qquad \textbf{Eq. 7}$$

the minimum standard deviation of proficiency assessment coherent with method reproducibility, $\hat{\sigma}_m$, can be calculated by the following equation (ISO 13528):

$$\hat{\sigma}_m = \sqrt{(0.5 \cdot s_L)^2 + \frac{s_r^2}{n}} \qquad \textbf{Eq. 8}$$

Therefore, when $\hat{\sigma}_{N37}$ is higher than $\hat{\sigma}_M$ the AQUILA N37 proposed value for the standard deviation for proficiency assessment is coherent with the reproducibility of the measurements in the exercise. Otherwise, the corresponding expected reproducibility standard deviations cannot be achieved in practice.

En values

As laboratories were requested to report uncertainty values for each concentration level, the evaluation of the laboratory performance was based on the E_n number as recommended by ISO/EC Guide 43-1:1997, A.2.1.4 item E. This number is calculated according to the following equation:

$$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}} \qquad \textbf{Eq. 9}$$

where U_{lab} and U_{ref} are the expanded uncertainties for the reported and reference value, respectively.

E_n number expresses the validity of the expanded uncertainty estimate associated with each result. The critical value for E_n number is 1. E_n numbers higher than 1 identify results that are incompatible

with the reference value after allowing for the stated uncertainties. The overall evaluation of the laboratory results should consider both bias and E_n value, because a low E_n value could be due to a large stated uncertainty.

RESULTS AND DISCUSSION

Data reporting

Although the intention of the participating laboratories was to report all levels and compounds included in the compared mixture, the black-out that occurred during the exercise caused several instruments to miss the analysis of some concentration step levels for a number of or even all the compounds. Figure 1 represents, for each participant, instrument and compound, the percentage of reporting data in each up and down series of concentration with respect to the total reporting data volume.

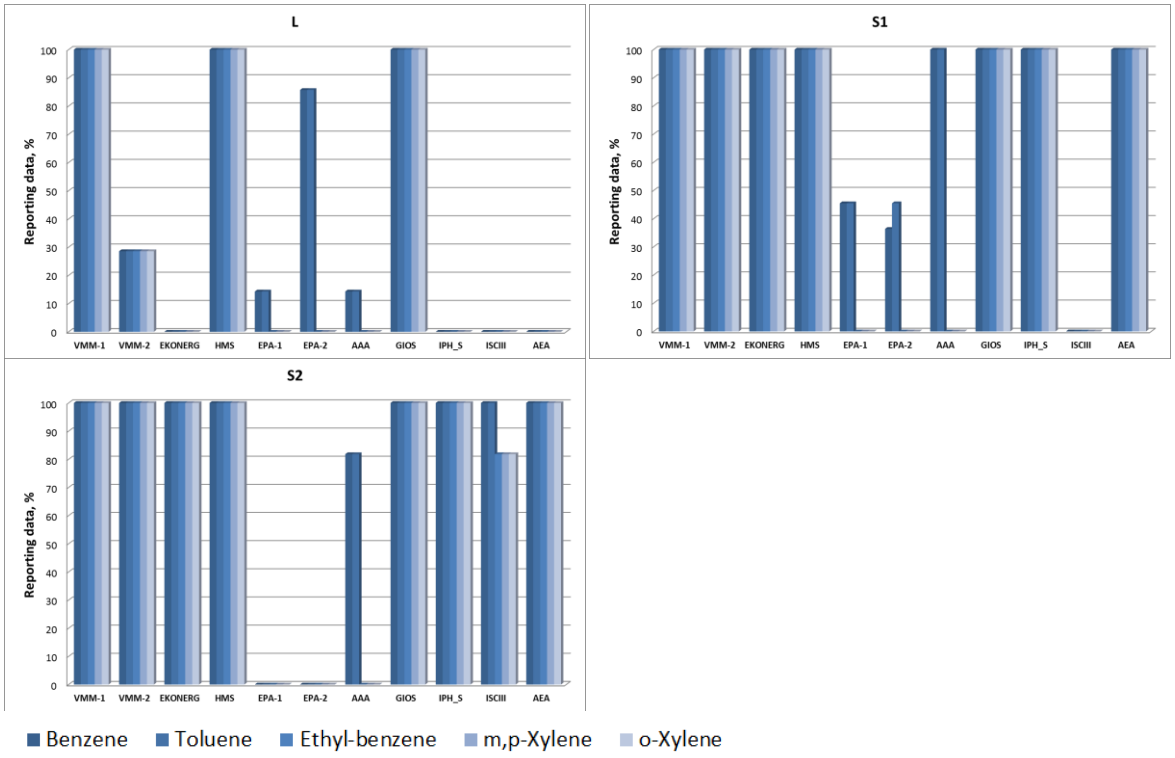


Figure 1.– Percentage of data compounds reported by the participating laboratories and the instruments in each testing series

Linearity test

Tables 5.I to 5.III show the results of the linearity test for the correlation between reported and reference values. Residuals were calculated by Eq. (1). In this table the percentage of residuals was

indicated for those values higher than 5 %. Values were highlighted in red when these were higher than 10 %. Linearity problems were identified mainly at the lowest concentration levels, eventually with higher incidence on the heaviest compounds. In general, an improvement of the linearity can be seen along the course of the inter-laboratory comparison from series L to S2, due to the stabilization time needed by the instruments after the black-out during the 2^{nd}-3^{rd} step of the L series.

Table 5.I.- Linearity test

	VMM1			VMM2			EKONERG			HMS		
Benzene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A	28.5	42.3	9.4	32.	70.7	74.2		27.2	22.1	81.1	8.8	7.3
2nd -A	-9.1	OK	-5.8	-	OK	OK		OK	OK	-	OK	OK
3rd -A		OK	OK		OK	OK		OK	OK		OK	OK
4th -A	OK	OK	OK	-	-5.4	-6.6		OK	OK	8.4	OK	OK
5th -A	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
6th	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
5th -B	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
4th -B	OK	OK	OK	-	OK	OK		OK	OK	9.0	OK	OK
3rd -B	8.9	OK	OK	7.2	OK	OK		OK	OK	22.1	OK	OK
2nd -B		OK	OK		7.7	8.4		OK	OK		OK	OK
1st -B		27.4	25.7		70.3	85.3		26.3	29.8		8.4	11.0
Toluene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A	21.2	27.5	12.1	40.	15.3	12.3		-	-76.8	-	40.0	-15.9
2nd -A	-25.0	-8.1	-10.5	-	-	-		-	-27.3	-	8.7	-9.3
3rd -A		-7.4	OK		OK	OK		-6.4	OK		7.1	OK
4th -A	OK	OK	OK	-	OK	OK		5.6	5.2	OK	OK	OK
5th -A	OK	OK	OK	-	OK	OK		9.0	8.5	OK	OK	OK
6th	OK	OK	OK	-	OK	OK		-6.7	-6.4			
5th -B	OK	OK	OK	-	OK	OK		9.4	8.9	OK	OK	OK
4th -B	OK	OK	OK	-	OK	OK		7.0	7.4	OK	-	OK
3rd -B	7.8	OK	OK	9.0	OK	OK		OK	OK	OK	9.7	OK
2nd -B			OK			OK			-17.3			OK
1st -B			30.0			37.0			-67.2			-5.3
Ethyl-benzene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A	OK	43.6	43.2	-	218.	235.		14.0	7.9	-	17.0	10.8
2nd -A	-31.2	17.6	-9.5	OK	6.5	6.5		-	-11.9	-	OK	OK
3rd -A		-	-8.8		-7.8	-8.8		OK	OK		OK	OK
4th -A	OK	OK	OK	-	-	-		OK	OK			
5th -A	OK	OK	OK	OK	OK	OK		OK	OK	OK	OK	OK
6th	OK	OK	OK	OK	OK	OK		OK	OK	OK	OK	OK
5th -B	OK	OK	OK	OK	OK	OK		OK	OK	OK	OK	OK
4th -B	OK	5.0	7.7	-	-6.0	-6.2		OK	OK	OK	OK	OK
3rd -B	OK	-6.3	OK	51.	OK	OK		OK	OK	OK	OK	OK
2nd -B			OK			21.4			OK			OK
1st -B			73.5			250.			27.5			28.2
m,p-Xylene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A	25.8	51.8	41.3	26.	159.	154.		8.0	11.8	59.0	39.2	23.8
2nd -A	-33.4	5.7	-19.6	-	OK	OK		-	-17.5	-	OK	-7.7
3rd -A		-	-14.0		-	-		OK	OK		-6.2	-7.9
4th -A	OK	OK	OK	-	-	-		OK	OK	OK	-6.9	OK
5th -A	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
6th	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
5th -B	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
4th -B	OK	8.9	9.7	-	-5.3	-5.2		OK	OK	10.4	OK	OK
3rd -B	OK	-	-10.8	5.8	-5.5	OK		OK	OK	9.6	OK	OK
2nd -B		-7.5	OK		7.2	9.8		OK	OK		OK	OK
1st -B		51.0	76.1		158.	180.		14.3	32.4		39.2	39.2
o-Xylene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A	99.5	26.4	5.4	43.	152.	151.		5.9	12.4	45.3	OK	OK
2nd -A	-30.6	-	-16.3	-	OK	OK		-9.4	-10.5	-	-7.0	-8.3
3rd -A		-6.5	-6.7		-	-		OK	OK		OK	OK
4th -A	OK	OK	OK	-	-	-		OK	OK	OK	OK	OK
5th -A	-5.3	-5.2	OK	-	OK	OK		OK	OK	OK	OK	OK
6th	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
5th -B	OK	OK	OK	-	OK	OK		OK	OK	OK	OK	OK
4th -B	OK	6.6	OK	-	-7.6	-8.1		OK	OK	OK	OK	OK
3rd -B	9.7	OK	OK	7.6	-5.5	-6.4		OK	OK	OK	OK	OK
2nd -B		OK	OK		7.0	8.9		OK	OK		OK	OK
1st -B		29.3	43.1		153.	164.		14.6	32.7		OK	13.5

Table 5.II.- Linearity test

	EPA1			EPA2			AAA			GIOS		
Benzene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A		-66.9		-202.3	-180.7		OK	-34.9	73.6	55.8	26.4	28.0
2nd -A		-6.9		-135.4	-22.8		OK	-20.3	19.7	-79.7	-7.2	-7.3
3rd -A		9.5			10.3			OK	21.9		OK	OK
4th -A		6.5		83.0	29.0		-91.2	OK	12.4	OK	OK	OK
5th -A		OK		40.9	OK		-90.9	OK	OK	OK	OK	OK
6th		-27.7		-7.7	OK		-90.8	OK	OK	OK	OK	OK
5th -B		-29.2		-23.9	OK		-90.9	OK	OK	OK	OK	OK
4th -B		-36.5		-30.8	-22.2		-91.2	5.2	14.7	5.1	OK	OK
3rd -B		-47.7		-94.1	-51.3		-91.8	OK	-83.1	16.2	OK	OK
2nd -B		-62.5			-89.9			-6.3	-75.4		-6.6	-6.0
1st -B		-135.5			-280.5			-27.5	66.8		26.4	30.2
Toluene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A		-65.3		-99.1	14.1		OK	-130.1	-21.3	OK	OK	-28.7
2nd -A		-13.2		-66.1	OK		OK	-41.6	OK	-92.5	-24.7	-27.3
3rd -A		8.9			OK			OK	25.6		-7.8	-8.7
4th -A		9.7		63.2	OK		-89.6	14.3	26.5	OK	OK	OK
5th -A		OK		27.7	OK		-89.0	6.2	7.1	OK	OK	OK
6th		-32.4		-5.2	-35.2		-88.9	-5.8	-6.7	OK	OK	OK
5th -B		-34.1		-16.8	-34.9		-89.0	7.0	8.0	OK	OK	OK
4th -B		-42.6		-20.1	-33.8		-89.6	19.0	30.4	12.5	9.8	10.6
3rd -B		-55.5		-49.4	-32.2		-90.3	OK	-79.1	15.4	OK	OK
2nd -B									-90.3			OK
1st -B									-127.6			9.3
Ethyl-benzene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A									OK	-26.0	OK	-31.0
2nd -A									OK	-110.1	-27.8	-32.1
3rd -A									OK		-8.3	-5.9
4th -A									OK	OK	OK	OK
5th -A									OK	-5.7	OK	-6.1
6th									OK	OK	OK	OK
5th -B									OK	OK	OK	OK
4th -B									OK	10.2	14.8	16.7
3rd -B									OK	8.5	7.4	12.4
2nd -B									OK			OK
1st -B									OK			31.9
m,p-Xylene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A									OK	29.3	25.5	-26.2
2nd -A									OK	-135.5	-26.7	-35.9
3rd -A									OK		-10.3	-9.5
4th -A									OK	OK	OK	OK
5th -A									OK	-7.1	-5.9	-6.2
6th									OK	OK	OK	OK
5th -B									OK	OK	OK	OK
4th -B									OK	6.9	15.3	16.5
3rd -B									OK	OK	11.0	14.9
2nd -B									OK		-5.8	OK
1st -B									OK		OK	40.1
o-Xylene	L	S1	S2	L	S1	S2	L	S1	S2	L	S1	S2
1st -A									OK	44.9	OK	-24.5
2nd -A									OK	-99.1	-29.3	-38.2
3rd -A									OK		-12.7	-13.2
4th -A									OK	OK	OK	OK
5th -A									OK	-7.1	OK	OK
6th									OK	OK	OK	OK
5th -B									OK	OK	OK	OK
4th -B									OK	11.3	16.5	17.9
3rd -B									OK	5.5	5.8	8.3
2nd -B									OK		-8.4	-5.4
1st -B									OK		OK	29.9

Table 5.III.- Linearity test

	IPH_S			ISCIII			AEA		
Benzene	L	S1	S2	L	S1	S2	L	S1	S2
1st -A		OK	-5.7			27.2		-69.8	-63.4
2nd -A		OK	OK			OK		-29.0	-25.8
3rd -A		OK	OK			OK		-5.3	-6.4
4th -A		OK	OK			OK		OK	OK
5th -A		OK	OK			OK		8.8	8.1
6th		OK	OK			OK		-6.8	-6.2
5th -B		OK	OK			OK		9.7	9.0
4th -B		OK	OK			OK		6.1	5.8
3rd -B		OK	OK			OK		OK	OK
2nd -B		OK	OK			OK		-17.5	-15.1
1st -B		OK	OK			38.6		-70.7	-56.3
Toluene	L	S1	S2	L	S1	S2	L	S1	S2
1st -A		49.2	40.1			OK		-230.0	-200.0
2nd -A		OK	OK			-11.5		-61.3	-36.5
3rd -A		OK	OK			-9.1		OK	15.4
4th -A		-5.6	-5.3			-5.2		25.3	45.1
5th -A		OK	OK			OK		11.2	-44.3
6th		OK	OK			OK		-8.9	8.8
5th -B		OK	OK			OK		8.4	8.8
4th -B		OK	OK			OK		34.4	52.3
3rd -B		OK	OK			OK		7.2	24.5
2nd -B			OK			OK			-16.3
1st -B			49.1			34.1			-170.1
Ethyl-benzene	L	S1	S2	L	S1	S2	L	S1	S2
1st -A		26.3	22.3			OK		22.5	-28.8
2nd -A		-9.3	-10.0			-60.0		-28.4	-24.6
3rd -A		OK	OK			-15.5		OK	OK
4th -A		6.1	5.8			8.4		OK	OK
5th -A		OK	OK			OK		OK	OK
6th		OK	OK			OK		OK	OK
5th -B		OK	OK			OK		OK	OK
4th -B		7.9	7.1			25.0		7.9	8.0
3rd -B		OK	OK			8.5		9.5	6.3
2nd -B			-5.7			-28.5			10.4
1st -B			30.0			OK			37.0
m,p-Xylene	L	S1	S2	L	S1	S2	L	S1	S2
1st -A		68.5	54.5			15.7		189.4	-53.4
2nd -A		OK	-11.4			-27.5		-27.9	-35.6
3rd -A		OK	OK			-9.2		OK	OK
4th -A		OK	OK			OK		OK	OK
5th -A		-5.6	OK			OK		OK	OK
6th		OK	OK			OK		OK	OK
5th -B		OK	OK			OK		OK	OK
4th -B		OK	OK			11.3		7.0	12.8
3rd -B		OK	OK			OK		OK	5.3
2nd -B		-6.1	-7.5			-12.7		-23.7	7.2
1st -B		44.8	67.6			15.7		-91.7	15.1
o-Xylene	L	S1	S2	L	S1	S2	L	S1	S2
1st -A		8.6	OK			28.2		17.9	-26.3
2nd -A		-18.8	-23.1			-62.5		-28.7	-29.9
3rd -A		-11.2	-9.4			-23.8		-9.8	-10.3
4th -A		6.5	OK			5.6		OK	OK
5th -A		OK	OK			OK		OK	OK
6th		OK	OK			OK		OK	OK
5th -B		OK	OK			5.9		5.6	5.0
4th -B		7.0	7.0			24.9		11.2	11.2
3rd -B		-8.5	-7.5			OK		5.4	7.8
2nd -B		-16.8	-17.4			-35.0		-5.0	OK
1st -B		OK	OK			28.2		OK	41.9

Comparison between reference and robust average value

Assigned values acting as reference can be compared to the robust average derived from the result of each concentration level. The robust average value, $\overline{C_i}^*$, and its standard deviation, s^*, is calculated according to ISO 13528 (see robust analysis in the Annex).

Assuming a normal distribution for the bias, $\overline{C}_i^* - C_{ref}$, the associated standard uncertainty is estimated as:

$$s_{bias} = \sqrt{\frac{(1.25 \cdot s^*)^2}{p} + u_{C_{ref}}^2} \qquad \textbf{Eq. 10}$$

where p is the number of participating laboratories.

The null hypothesis for a bias equal to zero can be evaluated using the two tails statistical test of normal distribution of the random variable, Z, defined as:

$$Z = \frac{\overline{C}_i^* - C_{ref}}{s_{bias}} \qquad \textbf{Eq. 11}$$

for which the probability function of the distribution for a confidence level of (1-α) is:

$$P(-Z1-\alpha/2 < Z < -Z1-\alpha/2) = 1 - \alpha \qquad \textbf{Eq. 12}$$

α represent the level of significance of the test. P values lower than 0.95 imply no significant bias and the bias becomes significant with the increase of the P value.

Tables 6.I to 6.III show the results of the statistical test. Significant biases with α values lower than 0.01 can occasionally be observed for lower concentration levels. The relatively high uncertainty associated with the reference values and the robust averages imply, in particular for the lowest concentrations, that no significant differences are found, even if sometimes high biases appear. It is, however, observed a general trend of over-estimation of concentrations during the different steps of decreasing concentration in each of the series, which becomes more evident for the heaviest compounds. This is probably due to the carry over and memory effect of the instrumentation.

In general, these results confirm the reference values and associated uncertainties as coherent with the robust average values of the inter-laboratory comparison.

Table 6.I.- Robust average value, level of significance and bias with respect to the reference value. L

Level	Benzene	α	Bias, %	Toluene	α	Bias, %
1ST-A	0.90	0.019■	-30.25	3.06	1.39E-02■	-35.45
2ND-A	2.10	0.066	-30.13	6.69	5.72E-04*	-36.53
3RD-A	5.14	0.661	2.00	17.91	0.672	1.34
4TH-A	10.50	0.655	3.51	35.64	0.986	0.05
5TH-A	28.55	0.244	-6.17	102.75	0.461	-3.80
6TH-A	49.20	0.889	-0.90	166.00	0.530	-5.49
5TH-B	28.58	0.302	-5.60	104.36	0.724	-1.82
4TH-B	9.60	0.396	-5.21	35.51	0.991	-0.07
3RD-B	4.91	0.664	-1.92	18.67	0.287	6.27
Level	Ethyl-benzene	α	Bias, %	m,p-Xylene	α	Bias, %
1ST-A	0.51	1.17E-02■	-44.85	0.70	0.451	-23.94
2ND-A	0.73	4.10E-04*	-63.88	0.74	0.054	-63.45
3RD-A	3.51	0.048	3.98	4.12	1.02E-06*	21.42
4TH-A	6.50	0.167	-4.42	6.75	0.865	-1.28
5TH-A	19.22	4.18E-03*	-5.80	20.02	0.110	-2.41
6TH-A	33.40	0.985	-0.06	34.29	0.737	2.59
5TH-B	20.23	0.780	-0.37	20.66	0.819	1.20
4TH-B	7.10	0.424	4.66	7.48	0.106	9.62
3RD-B	2.98	0.334	-11.15	3.03	0.453	-10.14
Level	o-Xylene	α	Bias, %			
1ST-A	0.61	0.818	10.92			
2ND-A	0.74	5.13E-03*	-63.52			
3RD-A	3.35	0.862	-1.83			
4TH-A	6.76	0.671	-1.74			
5TH-A	19.80	0.372	-3.97			
6TH-A	33.25	0.856	1.56			
5TH-B	20.74	0.809	1.08			
4TH-B	7.02	0.738	2.36			
3RD-B	3.33	0.814	-1.88			

*: 95-99 % confidence level, (1- α) ■: > 99% confidence level, (1- α)

Table 6.II.- Robust average value, level of significance and bias with respect to the reference value. S1

Level	Benzene	α	Bias, %	Toluene	α	Bias, %
1ST-A	1.13	0.599	8.84	4.23	0.495	10.26
2ND-A	2.69	5.81E-03*	-13.11	9.51	7.50E-05*	-12.40
3RD-A	4.85	0.171	-6.11	16.63	0.200	-8.08
4TH-A	9.91	0.111	-4.85	33.77	0.251	-7.34
5TH-A	29.92	0.177	-4.19	95.61	0.157	-12.55
6TH-A	50.64	0.598	-2.71	155.92	0.228	-14.77
5TH-B	30.63	0.414	-1.94	101.53	0.399	-7.13
4TH-B	10.44	0.888	0.31	37.01	0.816	1.53
3RD-B	5.18	0.959	0.17	18.92	0.408	4.60
2ND-B	3.06	0.809	-1.31	11.26	0.546	3.77
1ST-B	1.19	0.420	14.17	4.80	0.119	25.00
Level	Ethyl-benzene	α	Bias, %	m,p-Xylene	α	Bias, %
1ST-A	0.69	0.659	22.18	1.03	0.501	62.98
2ND-A	1.76	0.267	-13.01	1.88	0.458	-10.96
3RD-A	3.07	0.237	-9.03	3.21	0.499	-8.96
4TH-A	6.63	0.641	-2.34	6.89	0.682	-2.88
5TH-A	19.79	0.442	-2.84	20.77	0.564	-2.40
6TH-A	34.42	0.713	1.83	35.87	0.725	1.28
5TH-B	20.60	0.823	1.15	21.61	0.719	1.54
4TH-B	7.08	0.524	4.19	7.51	0.487	5.84
3RD-B	3.30	0.836	-2.13	3.49	0.950	-0.96
2ND-B	1.92	0.735	-4.95	2.01	0.814	-5.09
1ST-B	0.67	0.650	19.58	0.82	0.679	29.75
Level	o-Xylene	α	Bias, %			
1ST-A	0.74	0.864	7.93			
2ND-A	1.69	4.84E-03*	-23.72			
3RD-A	3.10	0.028	-15.93			
4TH-A	6.82	0.183	-8.30			
5TH-A	20.69	0.103	-7.24			
6TH-A	35.61	0.248	-5.55			
5TH-B	21.69	0.601	-2.77			
4TH-B	7.39	0.938	-0.63			
3RD-B	3.39	0.440	-8.05			
2ND-B	1.93	0.381	-12.94			
1ST-B	0.76	0.835	9.75			

*: 95-99 % confidence level, (1- α) ■ : > 99% confidence level, (1- α)

Table 6.III.- Robust average value, level of significance and bias with respect to the reference value. S2

Level	Benzene	α	Bias, %	Toluene	α	Bias, %
1ST-A	1.067	0.851	2.48	4.14	0.380	7.89
2ND-A	2.861	2.59E-06*	-7.73	9.96	0.025■	-8.26
3RD-A	5.073	0.439	-1.84	18.12	0.971	0.15
4TH-A	10.326	0.527	-0.82	36.93	0.744	1.32
5TH-A	30.914	0.606	-1.02	102.93	0.459	-5.86
6TH-A	51.532	0.803	-1.00	164.21	0.339	-10.24
5TH-B	31.109	0.842	-0.40	104.58	0.601	-4.34
4TH-B	10.566	0.526	1.48	38.93	0.193	6.82
3RD-B	5.151	0.921	-0.32	19.22	0.316	6.22
2ND-B	3.023	0.613	-2.50	11.43	0.425	5.33
1ST-B	1.137	0.589	9.17	4.64	0.248	20.87
Level	Ethyl-benzene	α	Bias, %	m,p-Xylene	α	Bias, %
1ST-A	0.49	0.712	-11.79	0.60	0.927	-5.63
2ND-A	1.43	9.88E-03*	-29.16	1.39	0.025■	-34.04
3RD-A	2.93	0.073	-13.13	2.90	0.206	-17.71
4TH-A	6.67	0.651	-1.83	6.61	0.326	-6.76
5TH-A	20.22	0.867	-0.74	20.41	0.413	-4.10
6TH-A	34.78	0.527	2.89	35.60	0.918	0.51
5TH-B	20.87	0.632	2.43	21.13	0.897	-0.69
4TH-B	7.27	0.297	7.00	7.20	0.871	1.49
3RD-B	3.25	0.691	-3.50	3.17	0.518	-10.07
2ND-B	1.78	0.406	-12.18	1.78	0.499	-15.98
1ST-B	0.67	0.658	20.28	0.82	0.695	29.35
Level	o-Xylene	α	Bias, %			
1ST-A	0.58	0.646	-16.54			
2ND-A	1.38	1.16E-03*	-37.51			
3RD-A	2.93	2.11E-02■	-20.65			
4TH-A	6.81	0.105	-8.37			
5TH-A	21.20	0.252	-4.95			
6TH-A	36.24	0.383	-3.89			
5TH-B	22.00	0.787	-1.35			
4TH-B	7.52	0.879	1.14			
3RD-B	3.31	0.264	-10.24			
2ND-B	1.75	0.211	-20.81			
1ST-B	0.78	0.781	13.59			

*: 95-99 % confidence level, (1- α) ■: > 99% confidence level, (1- α)

Blank levels

Figure 2 shows the concentrations and corresponding uncertainties (± 1 σ) reported by the participants during the zero air concentration levels (L-zero-up, S2-zero-up and S2-zero-down). As a median, depending on the compound and the instrument, these levels represent between 5 and 20 % of the 1st tested level of concentration. If considered as a blank level, these are in the range with the uncertainty associated to the 1st level of tested concentration.

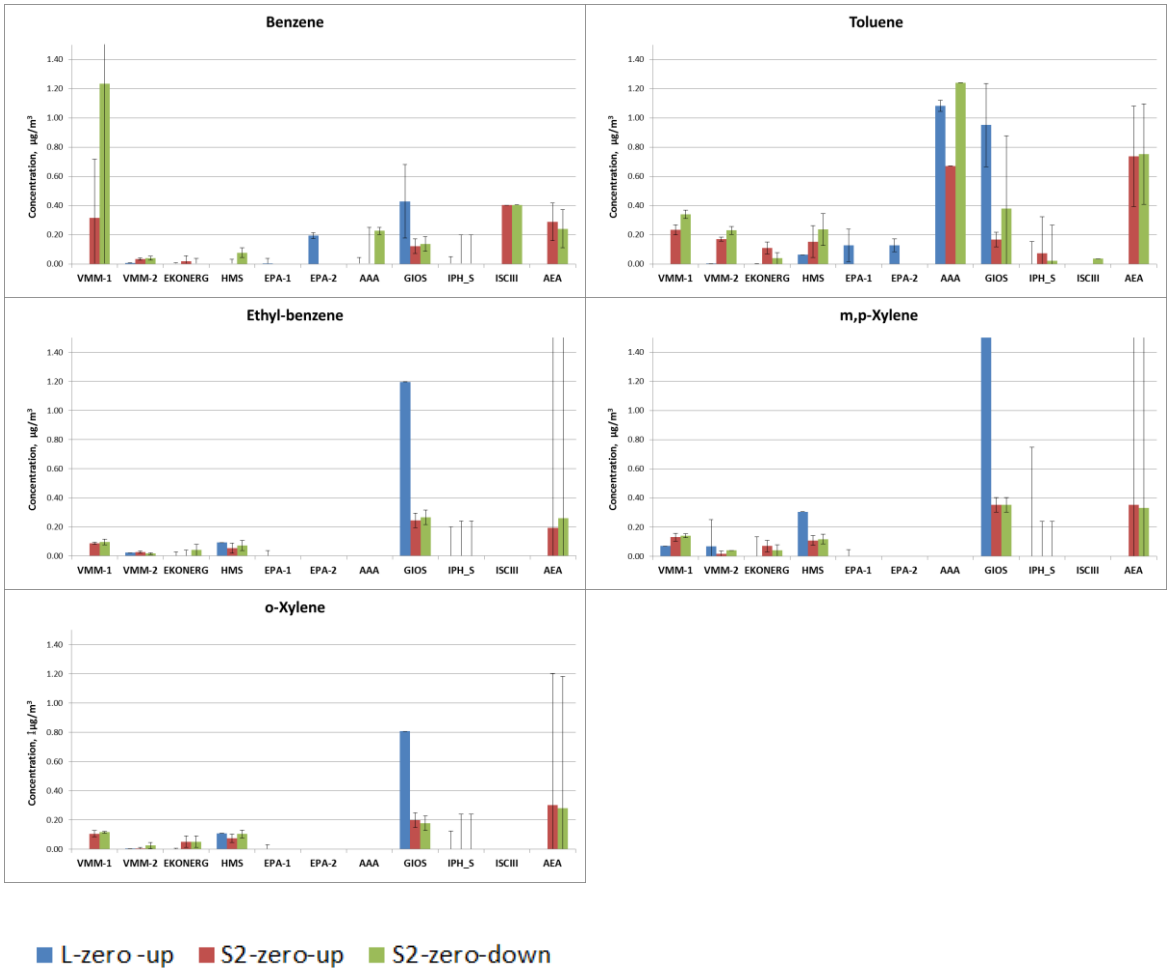
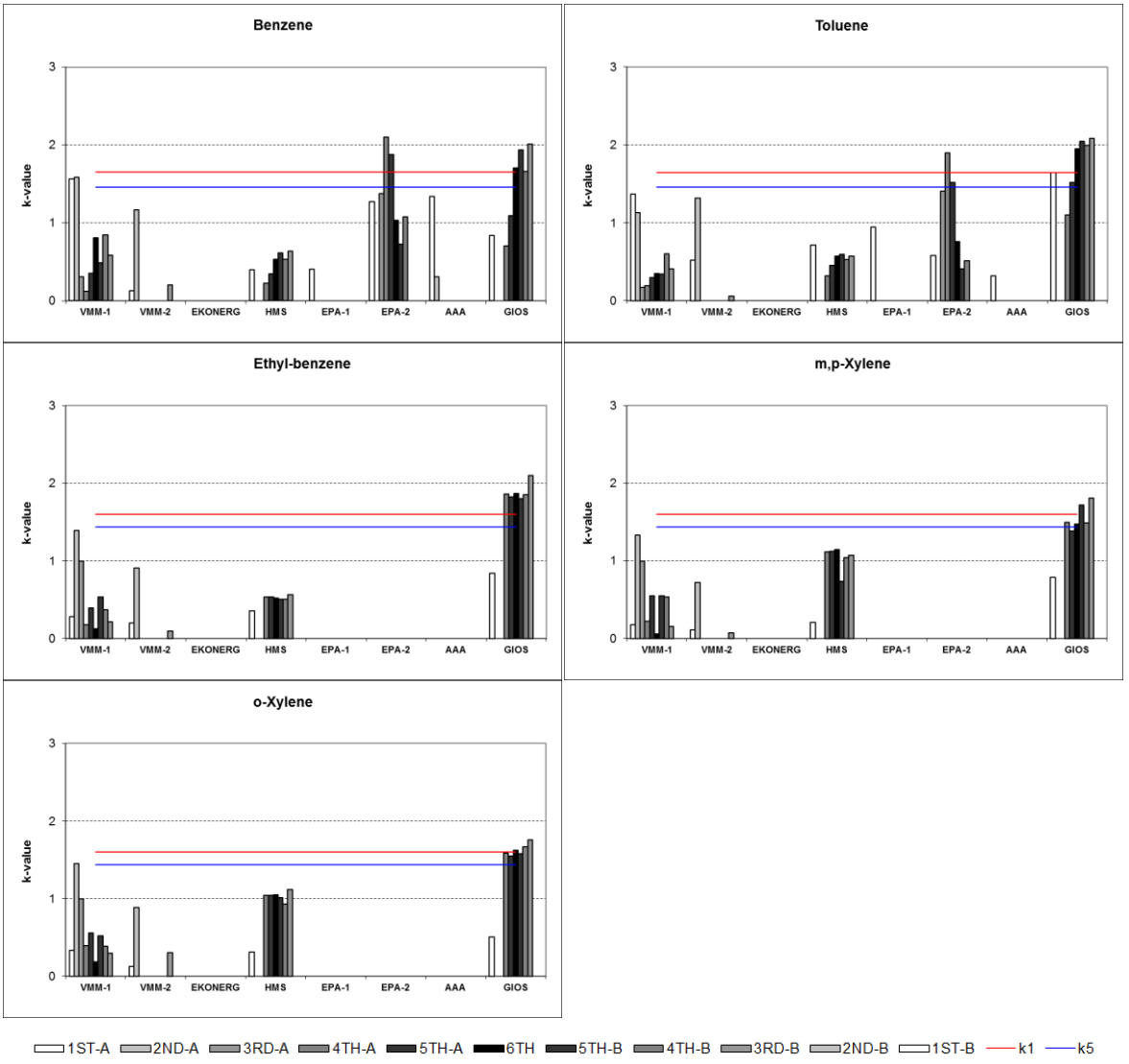


Figure 2.– Reported blank levels

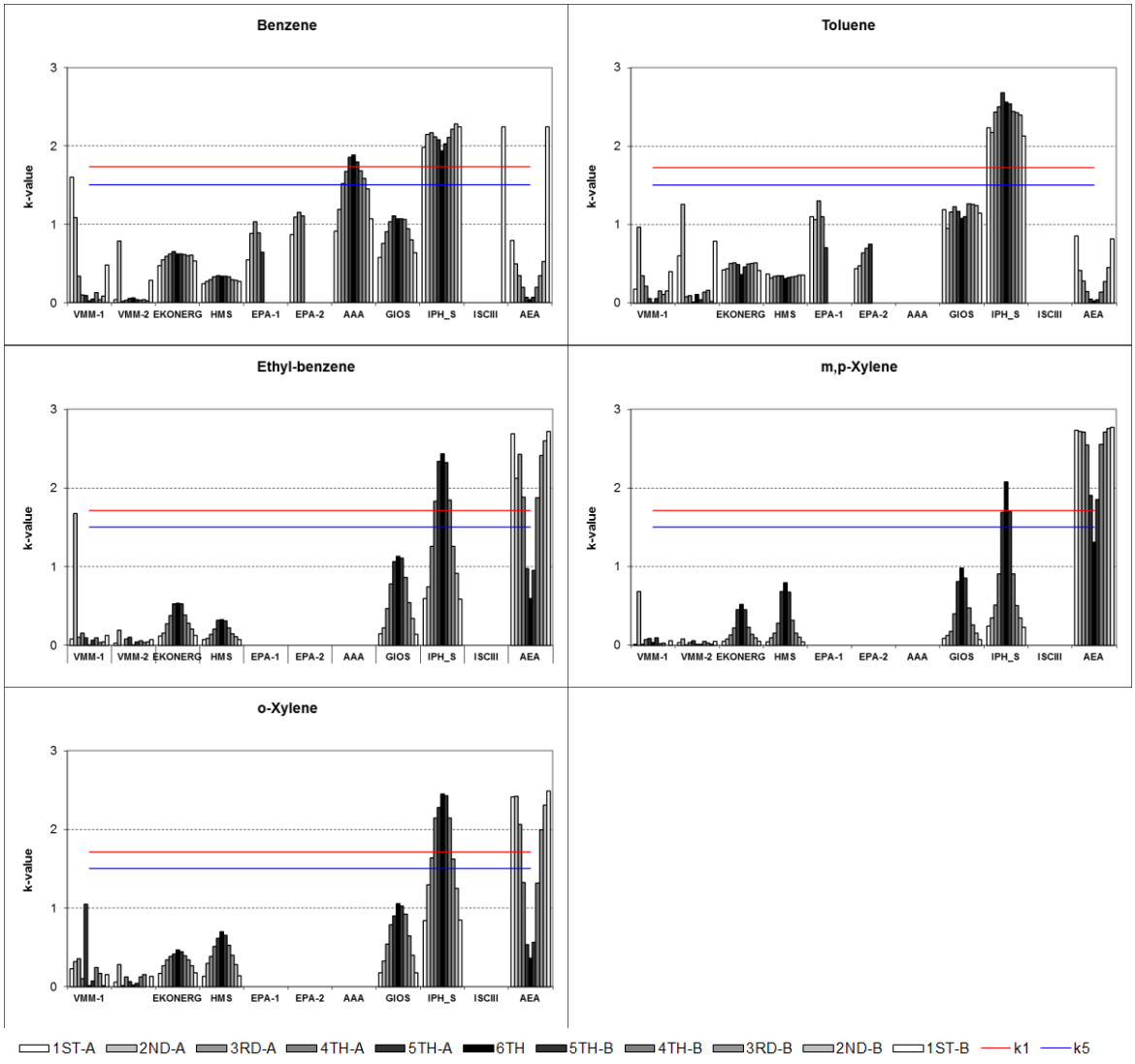
Outliers, repeatability, reproducibility and robustness of the method

As indicated in the previous section, repeatability and reproducibility standard deviation were calculated after elimination of the outliers identified by the k and h statistics. The results of these statistics are shown in figures 3.I.a-c and 3.II.a-c. The values of repeatability, reproducibility standard deviation and robustness of the three series are represented in figures 4.I to 4.III for each compound and tested concentration.



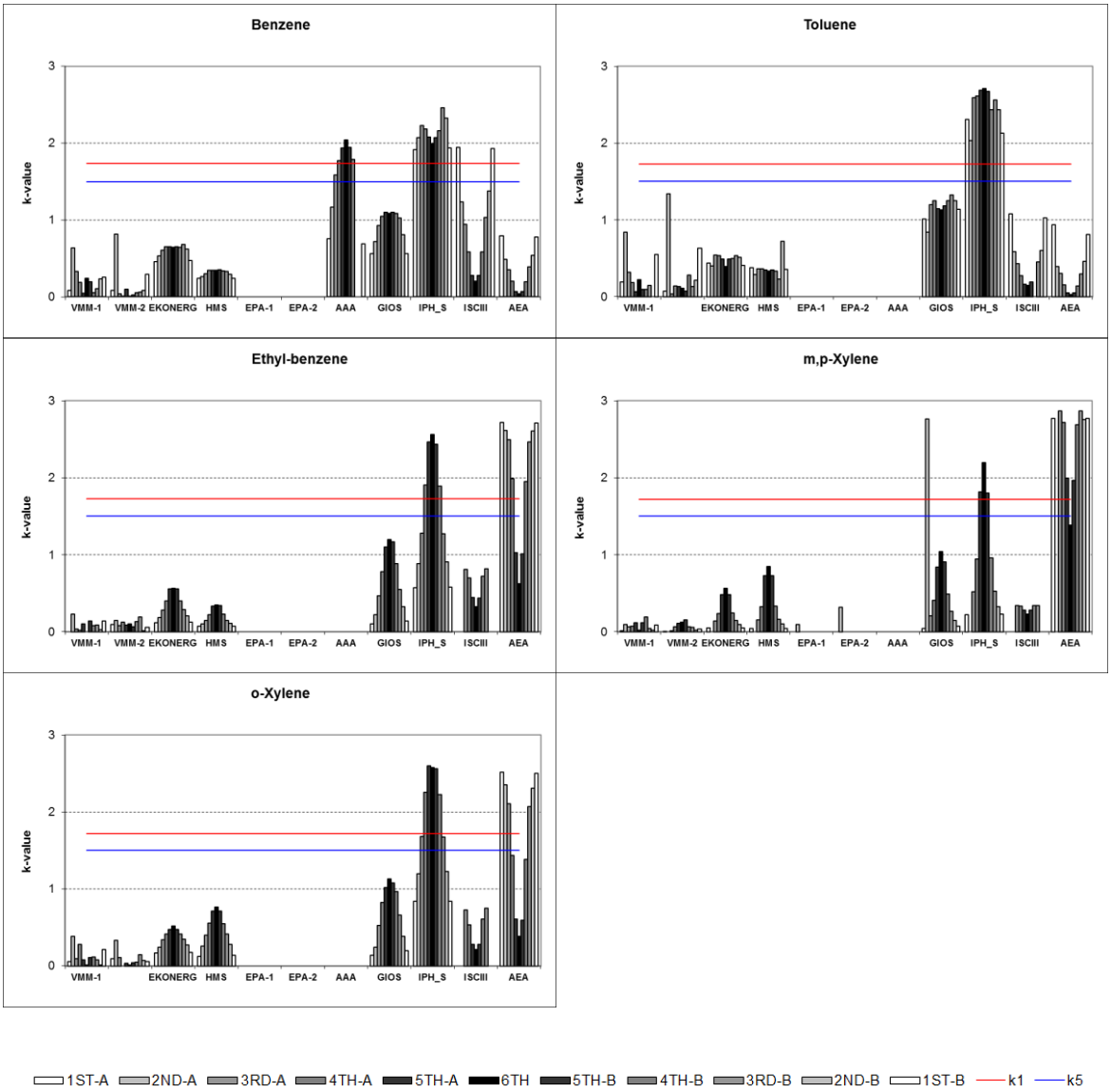
k1 and k5 corresponds to the 99 and 95 % confidence level)

Figure 3.I.a.– k-values for the L series



k1 and k5corresponds to the 99 and 95 % confidence level)

Figure 3.I.b.– k-values for the S1 series



k1 and k5 corresponds to the 99 and 95 % confidence level)

Figure 3.I.c.– k-values for the S2 series

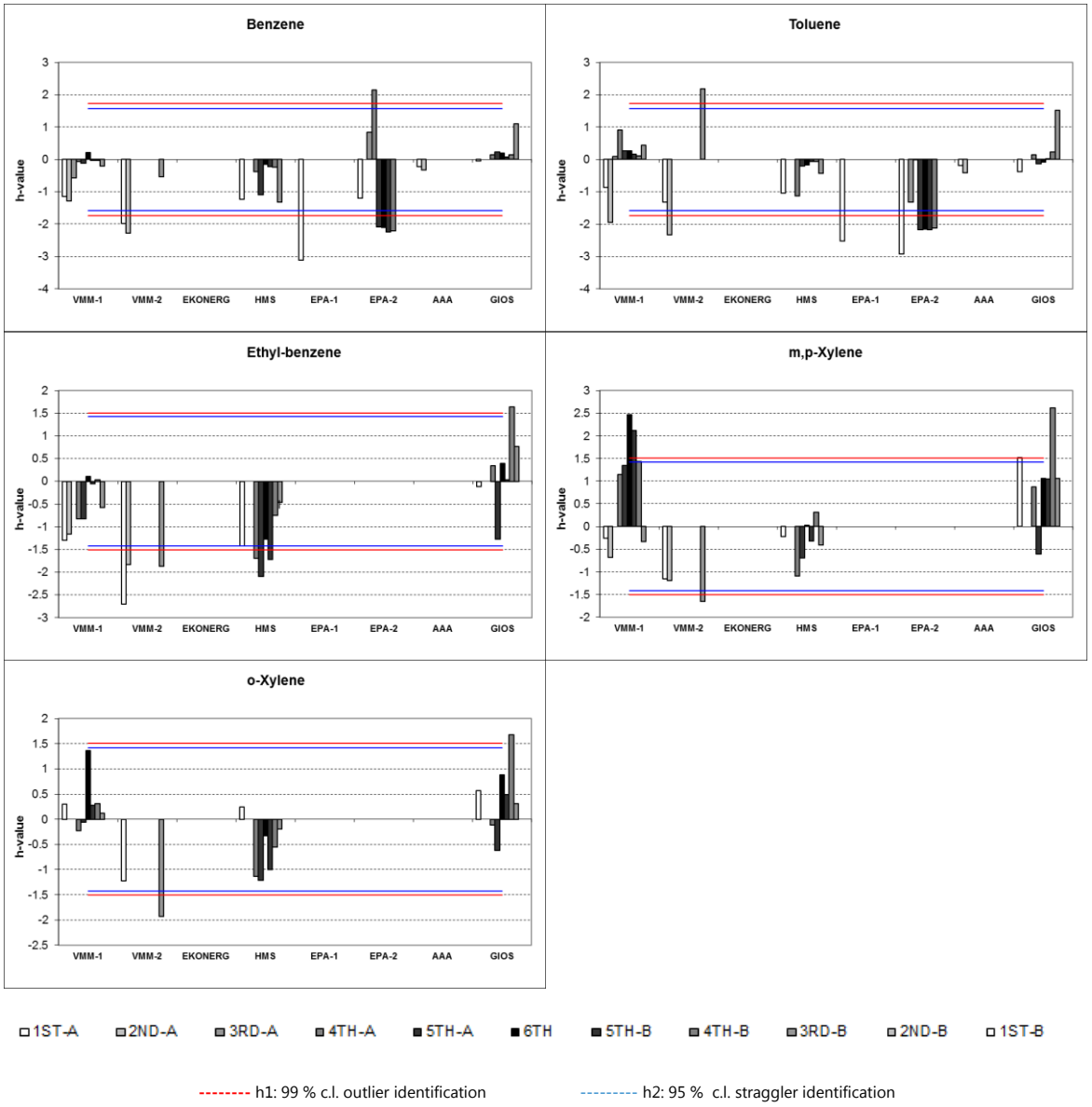


Figure 3.II.a.– h-values of the L series

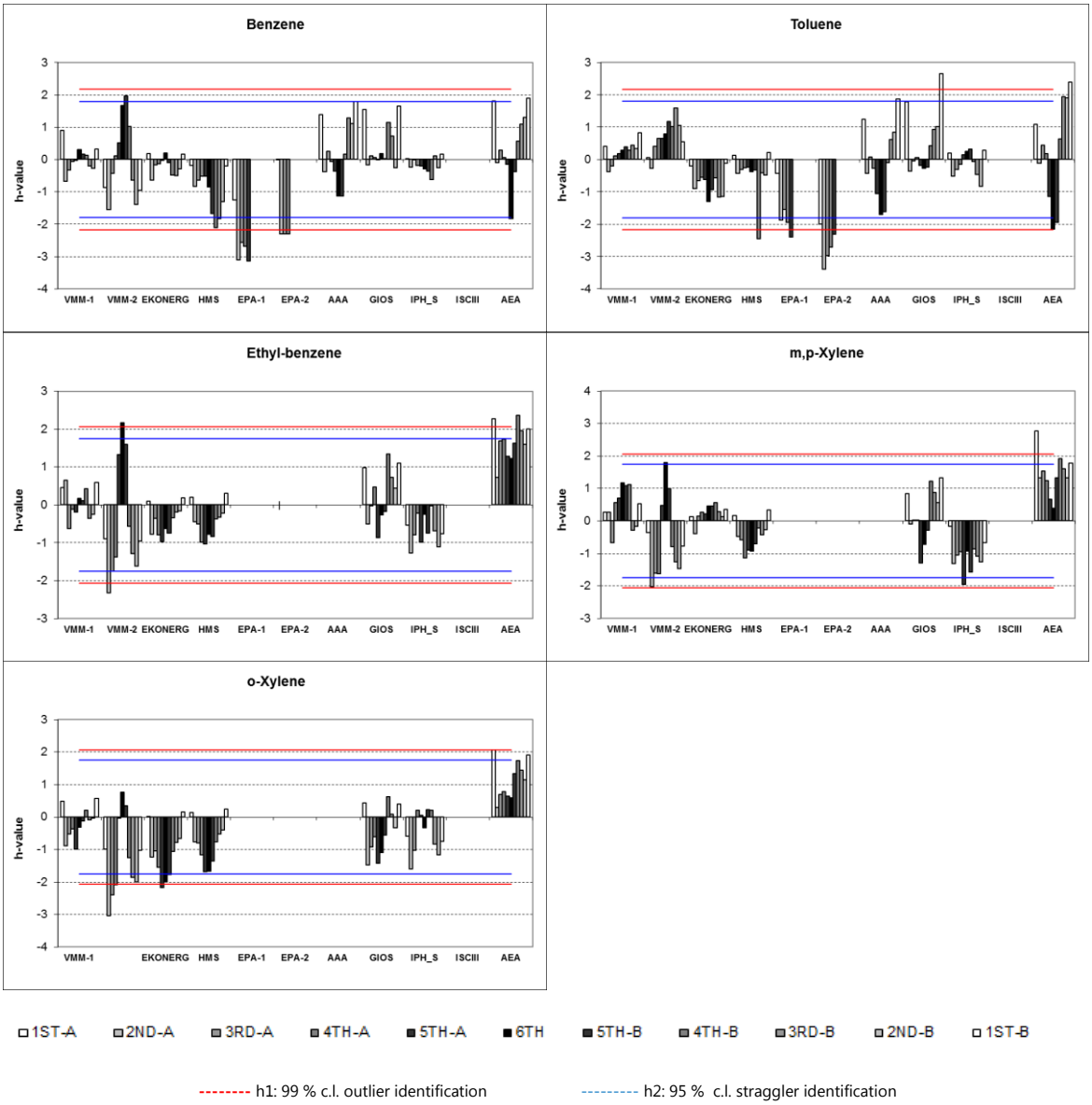


Figure 3.II.b.– h-values for the S1 series

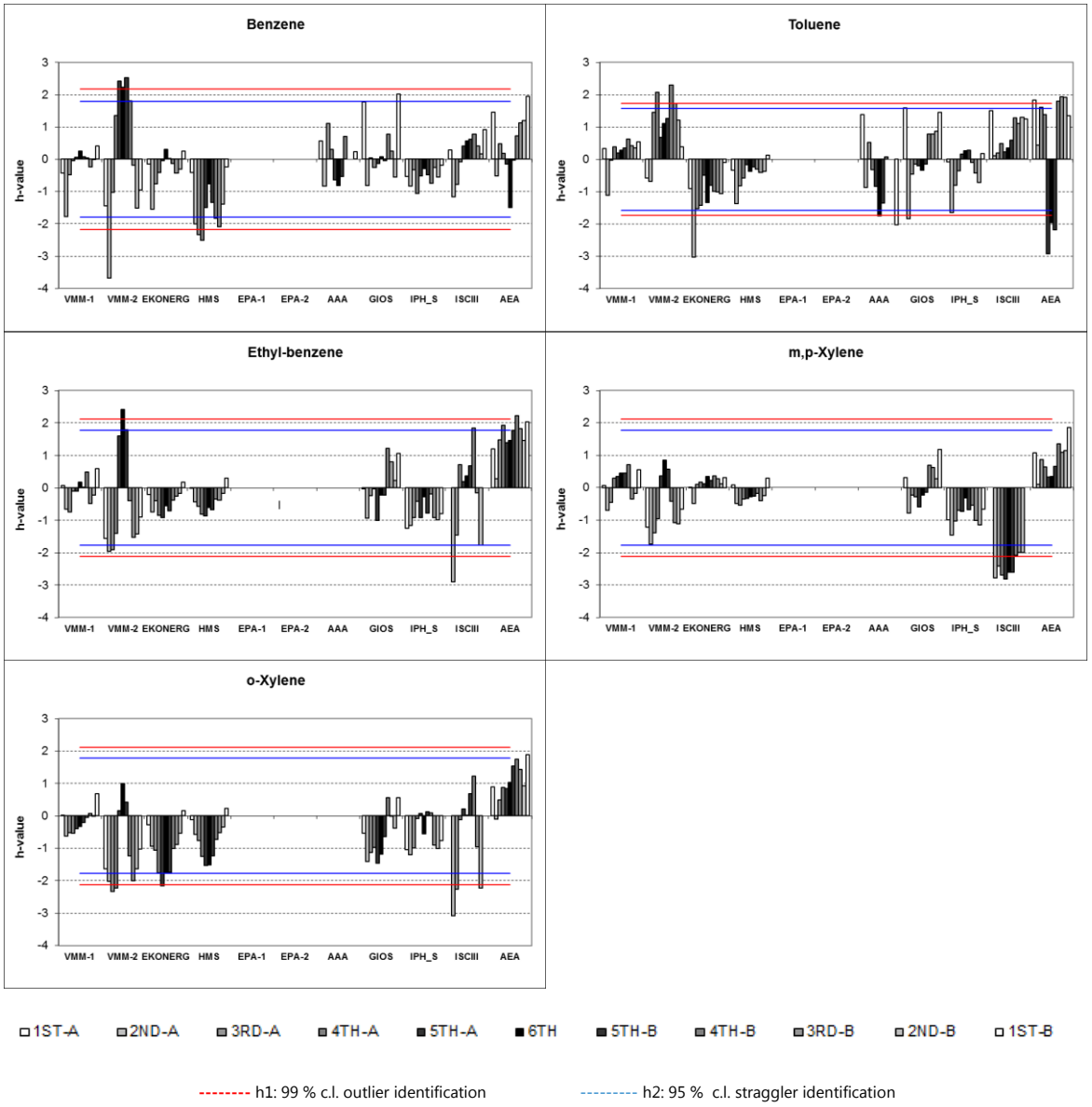


Figure 3.II.c.– h-values for the S2 series

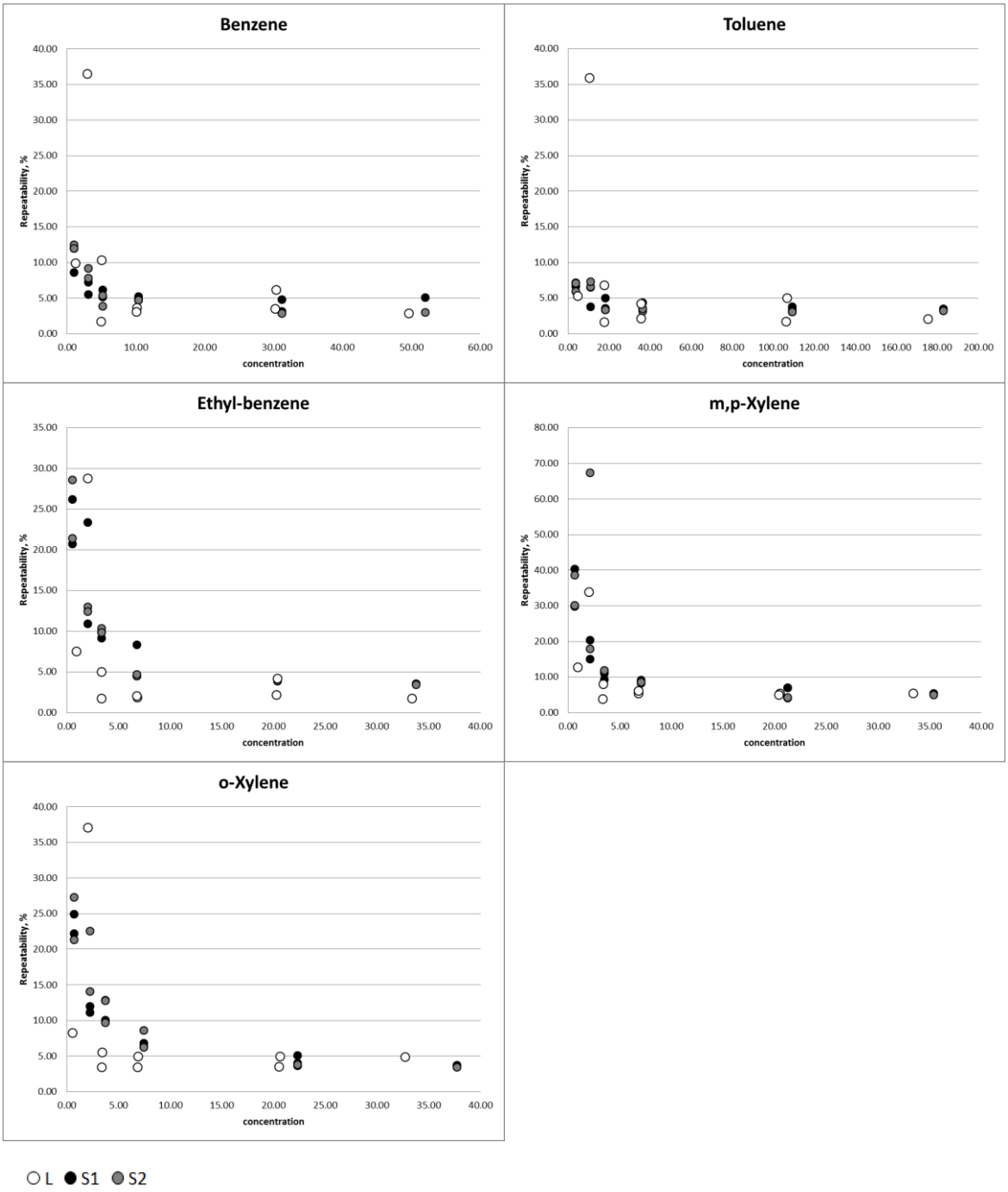


Figure 4.I.- Repeatability of the L, S1 and S2 series

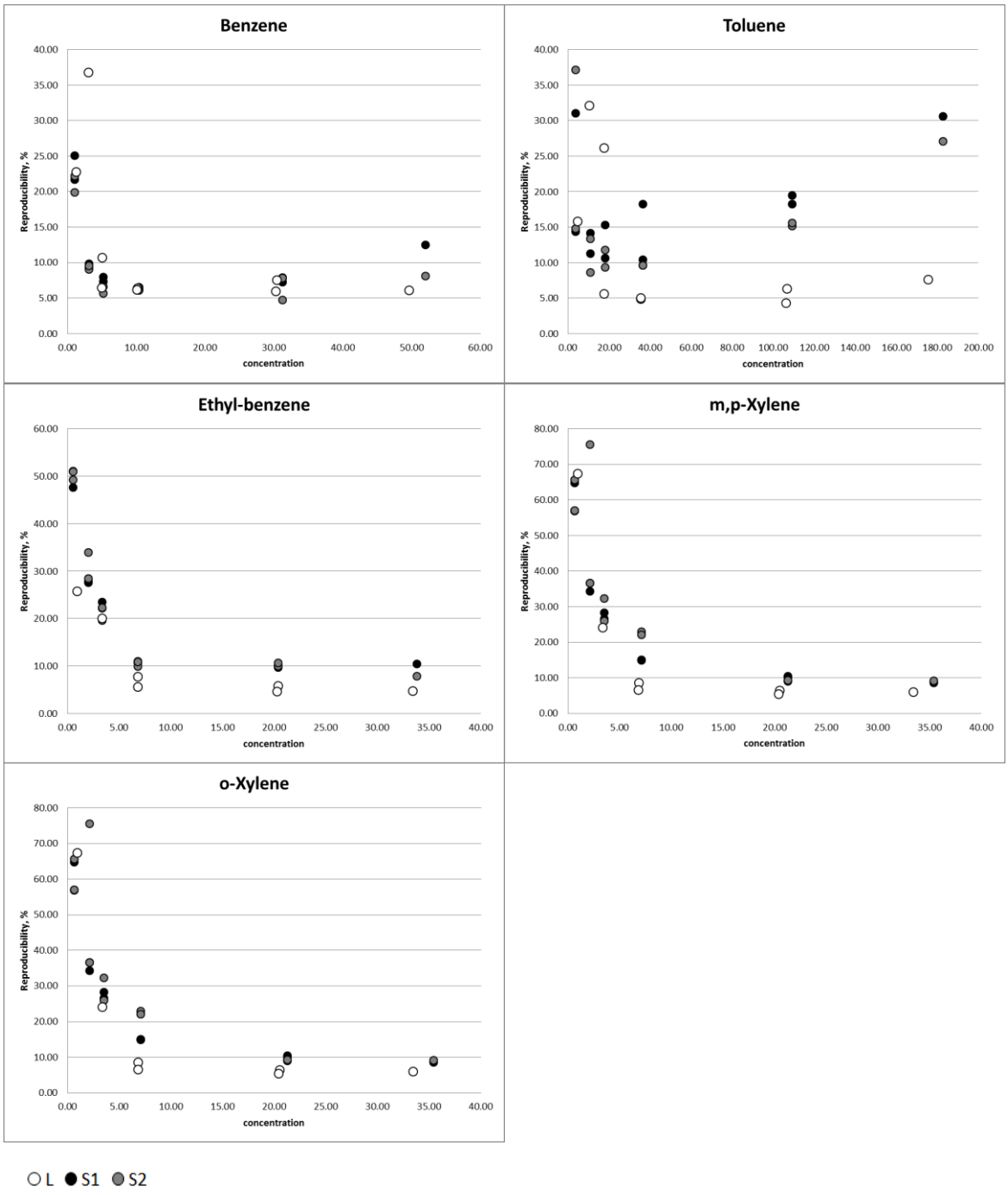


Figure 4.II.- Reproducibility of the(L, S1 and S2 series

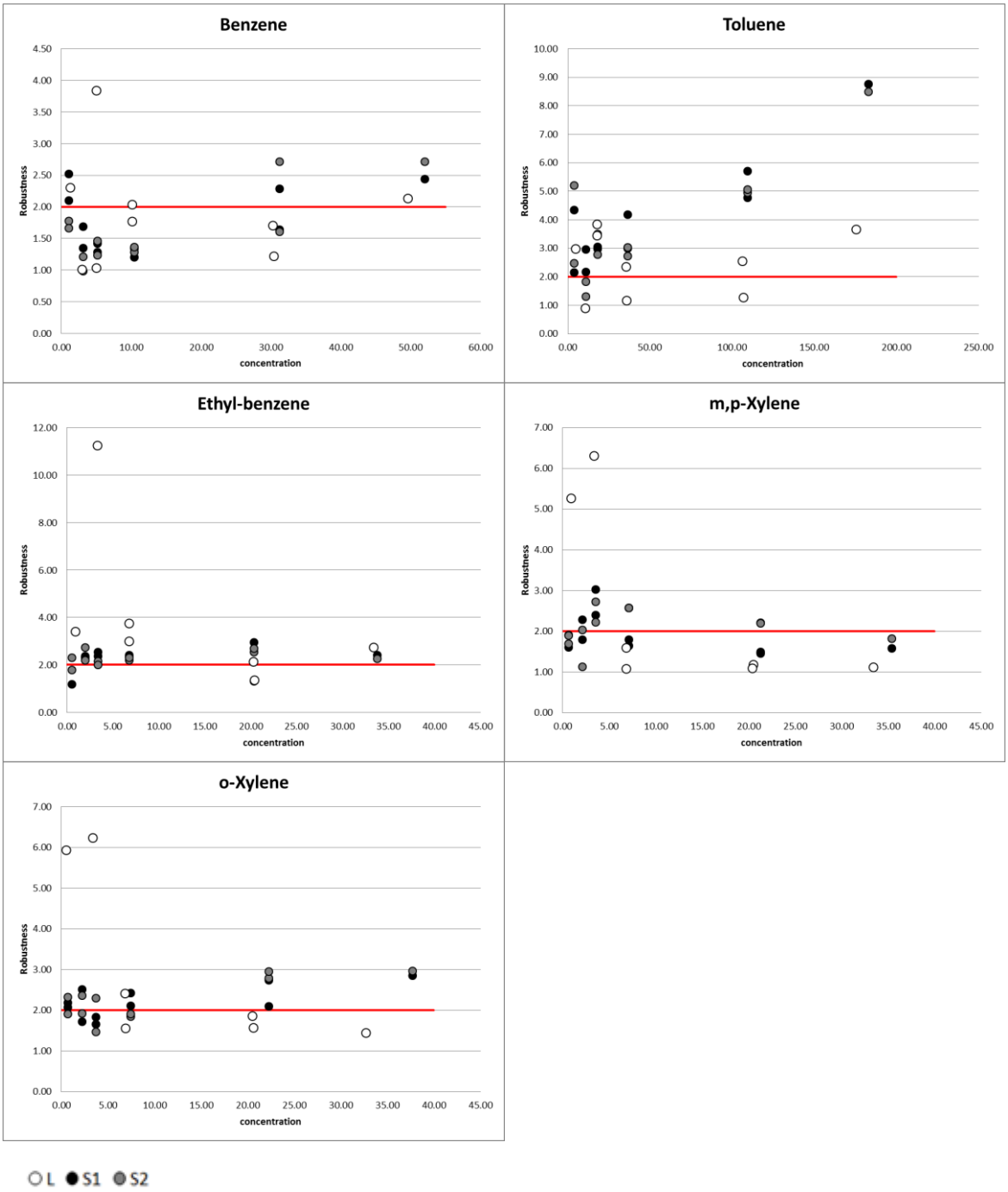


Figure 4.III- Robustness of the L, S1 and S2 series

As expected, figures 4.I and 4.II show that the values of repeatability and reproducibility increase with the decrease of the concentration. It is noted that the increase of the reproducibility value with concentration observed for toluene is probably due to a lack of linearity or a wrong calibration range of most of the instruments for this compound.

On the other hand, the robustness of the method (figure 4.III) seems to improve with respect to the previous two exercises (1st and 2nd BTEX inter-laboratory comparisons, EUR 22523EN, EUR 23792EN); this is probably due to the fact that, in this last inter-laboratory comparison, repeatability uncertainties were estimated for each concentration step by participants and used for input in the evaluation of results instead of the standard deviations of the n-individual measurements reported for concentration step in the past.

Table 7 shows, the average value of repeatability, reproducibility and robustness for each analyte during the three concentration series (L, S1 and S2). Again, it is noted the increase in the repeatability value of the method with respect to the 2nd BTEX inter-laboratory comparison and the improvement on the robustness of the method for all compounds and the benzene reproducibility in particular (see annex).

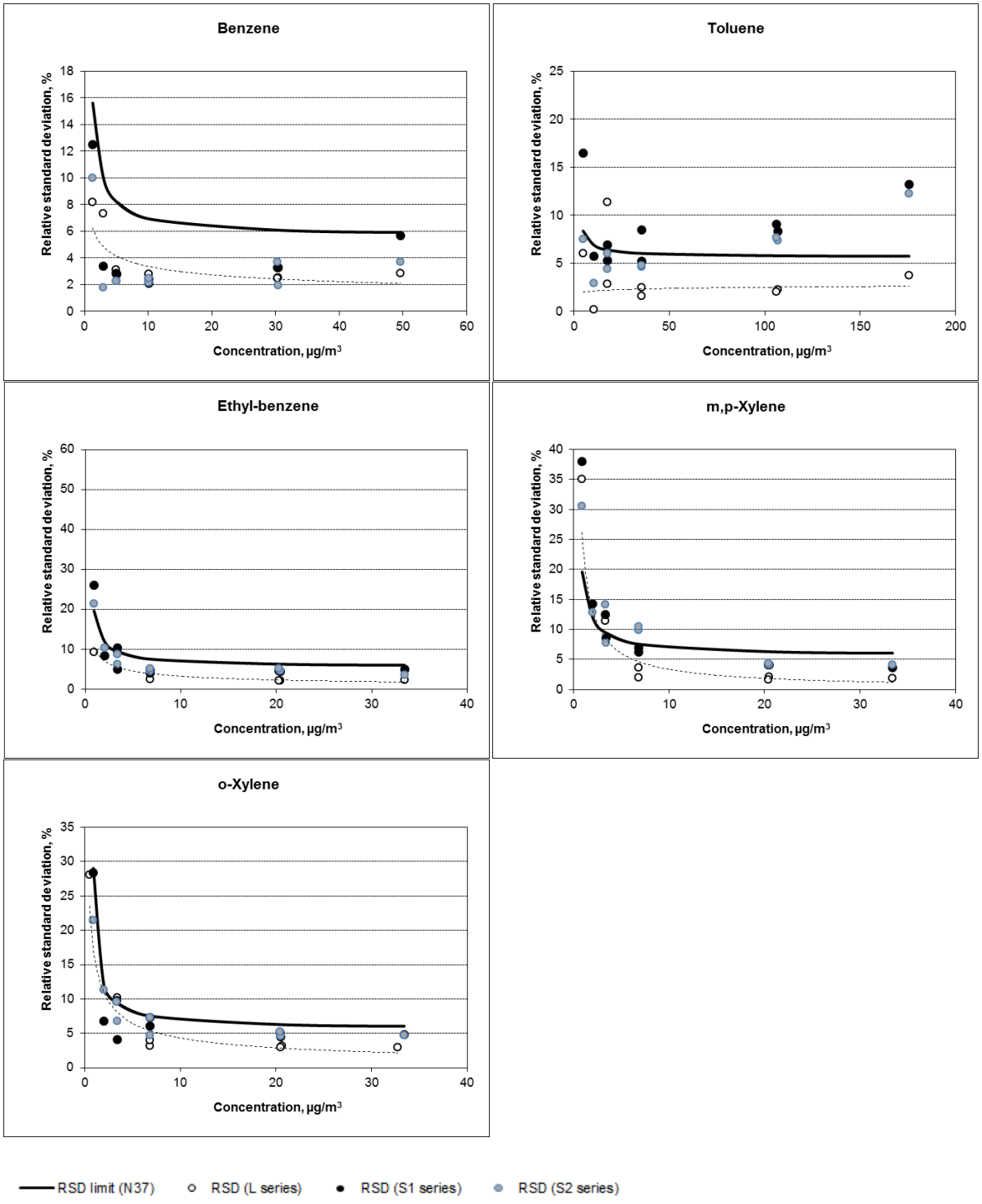
Table 7.- Average repeatability, reproducibility and γ values of the inter-laboratory exercise

	Repeatability, %	**Reproducibility, %**	**Robustness (γ)**
Benzene	4.7	7.9	1.7
Toluene	4.2	15.1	3.6
Ethyl-benzene	9.4	20.0	2.2
m,p-Xylene	9.3	26.6	2.8
o-Xylene	9.7	17.7	1.8

Standard deviation of the proficiency assessment N37

An overall evaluation of the method can be obtained from the comparison of the minimum acceptable standard deviation compatible with the reproducibility of the exercise and the standard deviation for proficiency assessment N37. In figure 5 both relative standard deviations are represented for the three concentration series and considered compound. For the estimation of the corresponding reproducibility values and standard deviation, outliers identified with the k and h test were excluded.

The minimum relative standard deviations calculated from the proficiency test agree with the N37 criteria for most of the compounds and concentrations, with the exception of toluene, for which the calculated minimum relative standard deviations compatible with the reproducibility of the tests become higher than the N37 criteria. This fact is probably due to the lack of linearity in the extrapolation of the calibration range at the higher concentrations in most of the instruments. Assuming that the calibration range was optimised for the analysis of benzene in the range from 0 to 50 µg/m^3, toluene was consequently out of range, as toluene concentrations were in a ratio of 3 to 1 with respect to benzene during the exercise. All laboratories were using BTEX standard mixtures with similar concentrations for all the compounds.



—— Relative standard deviation from AQUILA N37 proposal, $\hat{\sigma}_{N37}/C_{ref}\cdot 100$

--**O**-- Minimum relative standard deviation compatible with the reproducibility of the exercise, $\hat{\sigma}_{m}/C_{ref}\cdot 100$

Figure 5.- Minimum standard deviation compatible with reproducibility of the tests and standard deviation for proficiency assessment N37

Repeatability-score and E_n value

The individual evaluation of the laboratory test performance was carried out by means of the previously defined repeatability-score and E_n value. Results from the repeatability score are shown in figures 6.I to 6.III. Repeatability values over the red line correspond to reported uncertainties that exceed the criteria considered by the N37 and EN 14662-3.

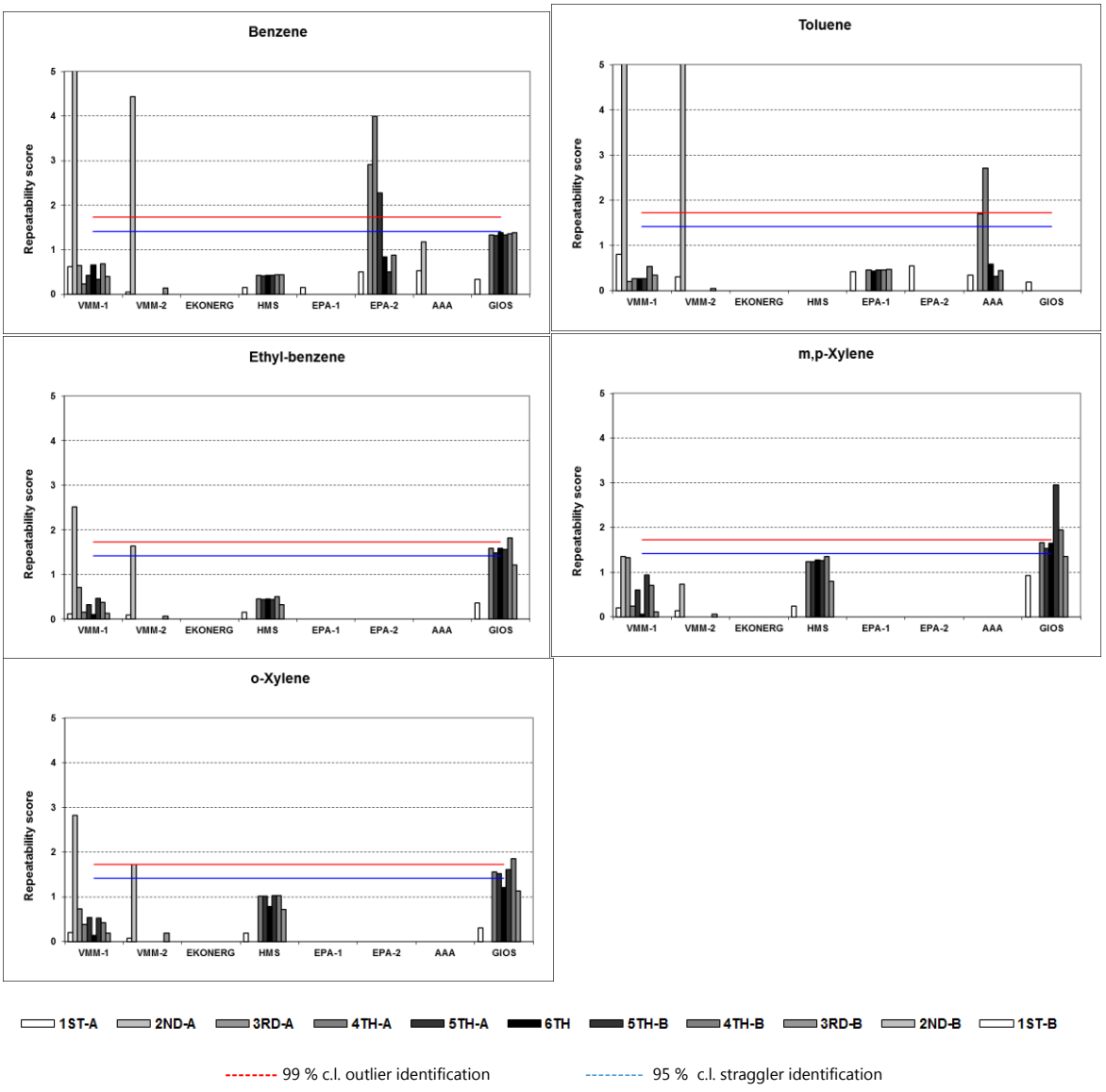


Figure 6.I.- Repeatability-score (N37) for the inter-laboratory comparison exercise. L series

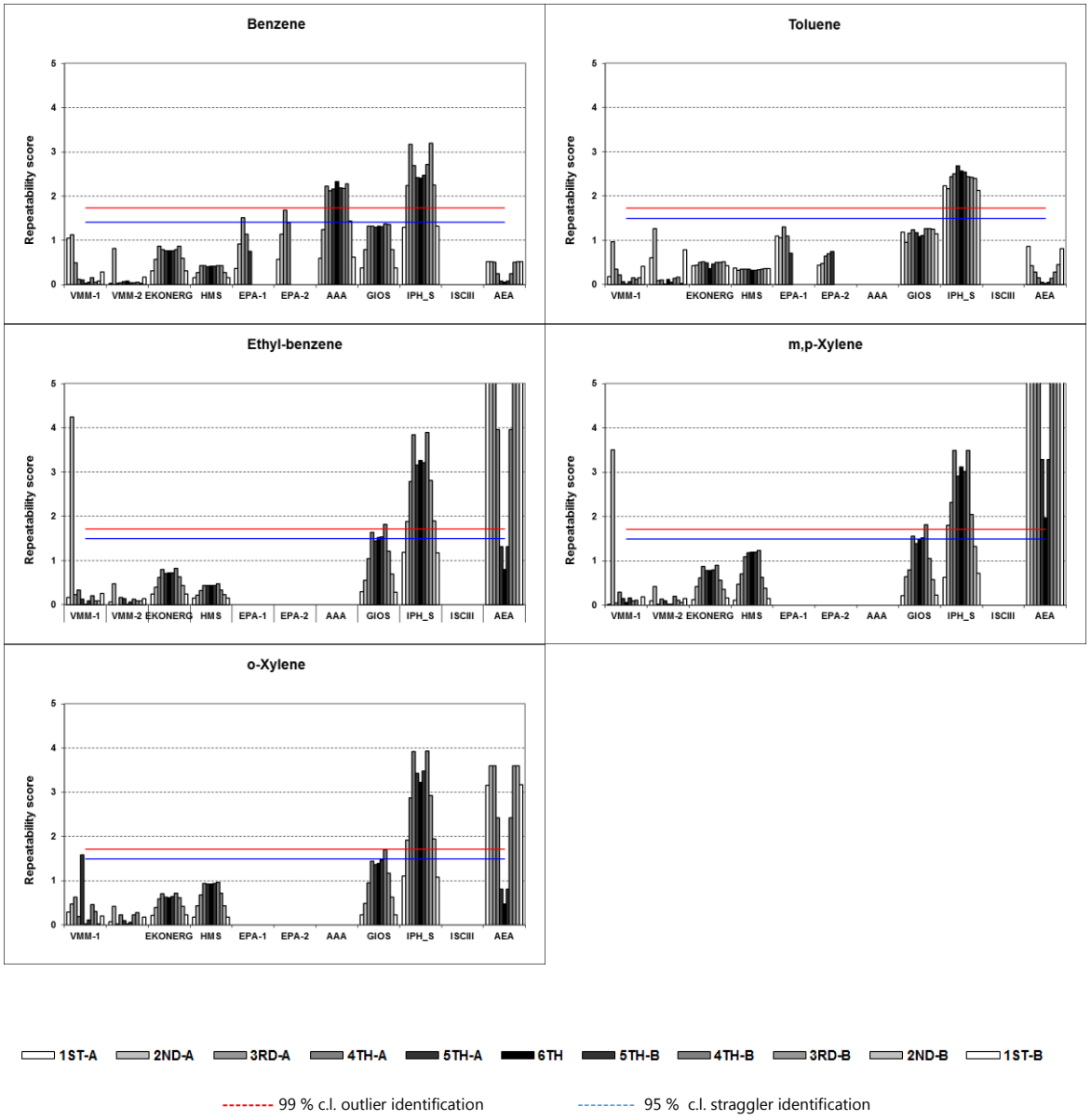


Figure 6.II.- Repeatability-score (N37) for the inter-laboratory comparison exercise. S1 series

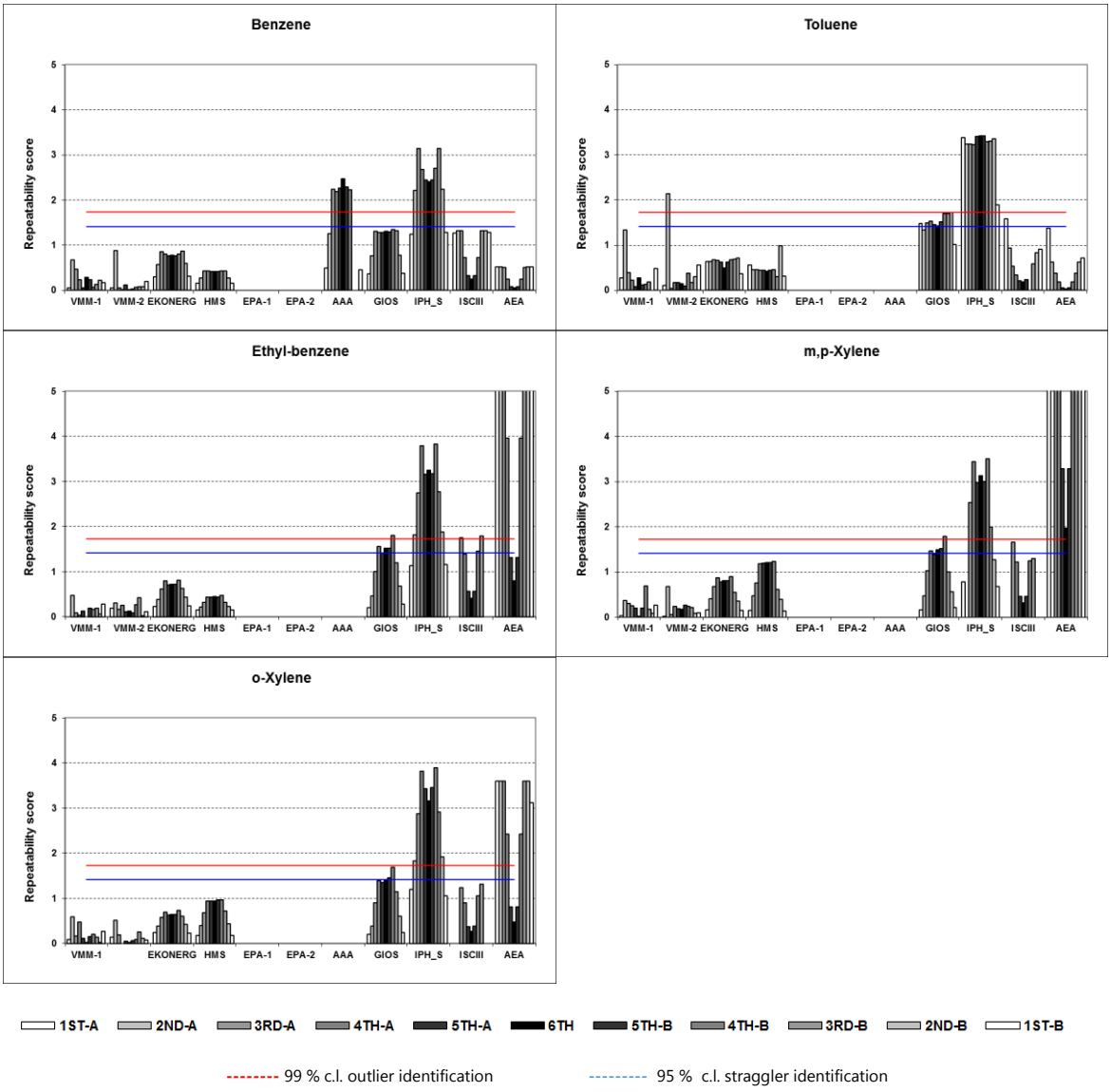


Figure 6.III.- Repeatability-score (N37) for the inter-laboratory comparison exercise. S2 series

E_n values have been determined for each reported concentration from each instrument. The results are shown in Tables 8.I to 8.V. Tables show in red the values that have not passed the E_n values (Action) test or the repeatability score (EU %). E_n warnings are instead highlighted in green.

Repeatability score and E_n value can be considered as supplementary test in the evaluation of the result. A high reported uncertainty could compensate a particular high bias and consequently pass the E_n value test. Such eventuality is eventuality identified by the repeatability score test. This is, for instance, the case of 1st-A level of the L series in VMM-2 for benzene in table 8.I.a. the 3rd –A level in EPA2 of table 8.I.b. or the 3rd-A to 3rd-B levels of AAA in table 8.I.c.

This type of statistical analysis provides an overview of the individual results provided by each laboratory. The interpretation of the actions and warnings is a matter for each laboratory and outside of the considerations of this report.

Table 8.I. a.- En value, bias and reported expanded uncertainty of the participants: benzene

Benzene		VMM-1					VMM-2					EKONERG				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.93	warning	-1.02	-27.78	33.45	0.67	Action	-3.78	-47.88	3.73					
1ST A	S1	1.28	OK	0.39	22.46	41.10	0.82	OK	-0.81	-21.72	1.72	1.09	OK	0.15	4.69	14.31
	S2	0.95	OK	-0.43	-8.75	2.95	0.74	warning	-1.42	-28.92	3.78	1.01	OK	-0.12	-2.99	14.85
	L	2.11	OK	-0.30	-29.92	143.09	1.42	OK	-0.72	-52.89	156.89					
2ND A	S1	2.80	OK	-0.53	-9.70	20.21	2.42	Action	-1.67	-22.12	16.98	2.82	OK	-0.99	-9.06	10.07
	S2	2.78	OK	-0.94	-10.34	12.23	2.44	Action	-1.52	-21.47	17.99	2.82	OK	-0.98	-9.05	10.07
	L	4.83	OK	-0.52	-4.17	6.76										
3RD A	S1	4.89	OK	-0.87	-5.38	5.19	4.81	Action	-1.84	-7.03	0.29	5.03	OK	-0.28	-2.68	8.91
	S2	5.06	OK	-0.37	-2.19	4.75	4.93	warning	-1.28	-4.61	0.57	4.99	OK	-0.37	-3.45	8.90
	L	10.28	OK	-0.28	-1.34	2.37	10.66					10.12				
4TH A	S1	10.40	OK	-0.54	-1.32	1.25	11.02	warning	1.09	2.33	0.39	10.23	OK	-0.34	-2.80	8.14
	S2	10.01	OK	-0.07	-0.16	2.31		Action	9.57	5.80	0.13		OK	-0.22	-1.74	8.13
	L	30.16	OK	-0.19	-0.89	4.37										
5TH A	S1	31.09	OK	-0.20	-0.47	1.05	34.89	Action	5.25	11.69	0.61	31.07	OK	-0.07	-0.52	7.64
	S2	31.37	OK	0.21	0.44	0.54	36.62	Action	7.38	17.23	0.97	31.14	OK	-0.04	-0.30	7.64
	L	53.07	OK	0.80	6.89	6.14										
6TH a	S1	53.84	Action	6.88	3.43	0.29	61.93	Action	21.50	18.97	0.66	53.21	OK	0.29	2.23	7.54
	S2	53.50	OK	0.93	2.77	2.83	65.14	Action	38.04	25.13	0.02	53.83	OK	0.44	3.42	7.54
	L	30.00	OK	-0.22	-0.93	3.41										
5TH B	S1	31.57	Action	1.77	1.07	0.58	35.26	Action	27.48	12.90	0.40	31.04	OK	-0.08	-0.62	7.64
	S2	31.41	OK	0.23	0.55	2.30	37.05	Action	23.52	18.63	0.23	31.31	OK	0.03	0.25	7.64
	L	10.05	OK	-0.09	-0.72	6.94										
4TH B	S1	10.48	OK	0.22	0.65	1.62	10.93	Action	1.97	4.93	0.38	10.17	OK	-0.28	-2.32	8.14
	S2	10.43	OK	0.06	0.17	0.67	11.35	Action	3.28	8.96	0.62	10.34	OK	-0.08	-0.69	8.12
	L	4.94	OK	-0.20	-1.34	4.11	4.84	OK	-0.63	-3.40	1.45					
3TH B	S1	5.11	OK	-0.25	-1.13	0.55	4.98	OK	-0.81	-3.64	0.56	5.02	OK	-0.30	-2.87	8.88
	S2	5.12	OK	-0.16	-1.03	1.37	5.13	OK	-0.14	-0.83	0.82	5.07	OK	-0.18	-1.90	8.88
	L															
2ND B	S1	3.04	OK	-0.24	-2.12	1.38	2.77	warning	-1.26	-10.83	0.51	3.03	OK	-0.18	-2.28	9.90
	S2	3.10	OK	0.00	-0.02	3.68	2.81	warning	-1.07	-9.54	1.50	3.04	OK	-0.15	-1.96	9.87
	L															
1ST B	S1	1.12	OK	0.25	7.57	12.68	0.81	OK	-0.77	-22.20	10.37	1.08	OK	0.12	3.73	14.44
	S2	1.12	OK	0.24	7.58	7.50	0.86	OK	-0.57	-17.88	11.46	1.09	OK	0.14	4.69	14.31

Table 8.I.b.- En value, bias and reported expanded uncertainty of the participants: benzene

Benzene		HMS					EPA-1					EPA-2				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.90	Action	-2.13	-29.70	8.69	0.32	Action	-5.37	-75.13	25.25	0.92	warning	-1.24	-28.80	27.48
1ST A	S1	1.00	OK	-0.16	-4.44	8.04	0.72	OK	-0.98	-31.33	25.17	1.04	OK	0.00	-0.11	27.31
	S2	0.96	OK	-0.38	-8.18	8.16										
	L															
2ND A	S1	2.73	Action	-2.60	-11.86	5.12	1.72	Action	-2.99	-44.44	26.70	2.08	Action	-1.79	-32.92	27.40
	S2	2.74	Action	-2.54	-11.73	5.12										
	L											5.35	OK	0.21	6.19	27.40
3RD A	S1	4.61	Action	-1.88	-10.74	4.77	2.96	Action	-2.75	-42.77	26.37	3.19	Action	-2.22	-38.37	27.38
	S2	4.63	Action	-1.89	-10.49	4.76										
	L	9.29	warning	-1.32	-7.96	4.73	4.49					5.33	warning	1.14	45.69	27.43
4TH A	S1	9.29	Action	-2.29	-10.81	4.74		Action	-4.94	-56.92	26.31		Action	-3.44	-48.81	27.39
	S2	9.34	Action	-2.52	-10.74	4.73						14.78				
	L	27.73	Action	-1.96	-8.86	4.62						25.31	OK	-0.74	-16.83	27.41
5TH A	S1	27.53	Action	-2.60	-11.85	4.58	8.86	Action	-9.20	-71.65	26.42					
	S2	27.91	Action	-2.33	-10.66	4.59										
	L	47.20	OK	-0.70	-4.94	4.58						15.24	Action	-6.88	-69.31	27.41
6TH a	S1	46.98	Action	-2.34	-9.74	4.60										
	S2	47.64	Action	-2.00	-8.48	4.58										
	L	27.88	Action	-1.61	-7.92	4.60						5.57	Action	-14.47	-81.59	27.40
5TH B	S1	27.79	Action	-2.69	-11.01	4.61										
	S2	28.14	Action	-2.34	-9.92	4.62										
	L	9.38	warning	-1.17	-7.39	4.71						3.24	Action	-6.86	-68.00	27.44
4TH B	S1	9.35	Action	-2.09	-10.25	4.71										
	S2	9.47	Action	-1.82	-9.06	4.65										
	L	4.59	warning	-1.22	-8.32	4.81										
3TH B	S1	4.63	Action	-1.69	-10.43	4.75										
	S2	4.68	warning	-1.26	-9.37	4.70										
	L															
2ND B	S1	2.79	warning	-1.05	-10.19	5.03										
	S2	2.83	OK	-0.89	-8.79	4.95										
	L															
1ST B	S1	0.99	OK	-0.17	-4.82	8.07										
	S2	1.00	OK	-0.14	-4.43	8.04										

Table 8.I.c.- En value, bias and reported expanded uncertainty of the participants: benzene

Benzene		AAA					GIOS					IPH_S				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	1.22	OK	-0.22	-5.33	21.81	1.27	OK	-0.07	-1.23	13.15					
1ST A	S1	1.40	OK	0.89	34.75	21.24	1.44	warning	1.20	38.59	13.03	1.04	OK	0.00	0.08	62.38
	S2	1.16	OK	0.36	11.22	21.24	1.41	warning	1.32	35.43	13.05	0.93	OK	-0.17	-10.67	67.10
	L	2.78	OK	-0.38	-7.58	21.18						2.93				
2ND A	S1	2.94	OK	-0.27	-5.35	21.19	3.02	OK	-0.19	-2.48	13.03	2.99	OK	-0.10	-3.48	37.35
	S2	2.95	OK	-0.24	-4.89	21.23	2.95	OK	-0.38	-4.76	13.00	2.95	OK	-0.14	-4.86	37.56
	L															
3RD A	S1	5.39	OK	0.19	4.35	21.29	5.27	OK	0.14	1.87	12.99	5.17	OK	0.00	-0.01	31.73
	S2	5.43	OK	0.22	5.01	21.26	5.18	OK	0.01	0.17	13.02	5.09	OK	-0.05	-1.49	31.86
	L						10.54	OK	0.21	2.99	13.00					
4TH A	S1	10.28	OK	-0.06	-1.28	21.50	10.30	OK	0.09	1.23	13.00	9.94	OK	-0.15	-3.92	27.99
	S2	10.55	OK	0.06	1.28	21.53	10.45	OK	-0.08	-1.06	13.01	10.57	OK	-0.17	-4.53	28.03
	L						30.98	OK	0.13	1.80	13.01					
5TH A	S1	28.65	OK	-0.38	-8.26	23.56	31.12	OK	-0.03	-0.37	13.00	29.84	OK	-0.18	-4.45	25.34
	S2	29.83	OK	-0.20	-4.51	23.76	30.94	OK	-0.07	-0.93	13.00	30.08	OK	-0.15	-3.71	25.33
	L						52.98	OK	0.45	6.71	13.02					
6TH a	S1	45.38	OK	-0.55	-12.82	26.76	53.12	OK	0.15	2.05	13.00	50.39	OK	-0.13	-3.19	24.80
	S2	47.27	OK	-0.37	-9.19	27.18	52.47	OK	0.06	0.81	13.00	50.39	OK	-0.13	-3.19	24.79
	L						31.13	OK	0.21	2.80	13.00					
5TH B	S1	28.92	OK	-0.34	-7.41	23.60	31.27	OK	0.01	0.12	13.00	30.49	OK	-0.10	-2.39	25.31
	S2	30.00	OK	-0.17	-3.96	23.78	31.12	OK	-0.03	-0.36	13.00	30.11	OK	-0.15	-3.60	25.33
	L						10.54	OK	0.29	4.15	13.04					
4TH B	S1	10.49	OK	0.04	0.78	21.52	10.99	OK	0.40	5.53	13.00	10.10	OK	-0.11	-2.98	27.95
	S2	10.78	OK	0.16	3.54	21.54	10.81	OK	0.28	3.81	13.01	10.03	OK	-0.13	-3.65	27.99
	L						5.35	OK	0.46	6.88	13.01					
3TH B	S1	5.55	OK	0.32	7.35	21.27	5.38	OK	0.29	4.17	13.00	5.20	OK	0.02	0.65	31.68
	S2						5.23	OK	0.08	1.10	13.01	5.11	OK	-0.03	-1.10	31.81
	L															
2ND B	S1	3.37	OK	0.35	8.68	21.25	3.04	OK	-0.13	-1.93	13.02	3.04	OK	-0.06	-2.06	37.14
	S2						2.99	OK	-0.23	-3.54	12.97	2.99	OK	-0.09	-3.50	37.37
	L															
1ST B	S1	1.48	warning	1.03	42.15	21.22	1.44	warning	1.17	38.59	13.03	1.08	OK	0.06	3.92	61.00
	S2	1.09	OK	0.12	4.41	21.16	1.43	warning	1.07	37.64	12.98	1.01	OK	-0.05	-3.28	63.75

Table 8.I.d.- E_n value, bias and reported expanded uncertainty of the participants: benzene

Benzene		ISCIII					AEA				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L										
1ST A	S1						1.51	warning	1.24	45.41	17.17
	S2	1.10	OK	0.09	5.85	57.62	1.35	OK	0.91	29.38	19.30
	L										
2ND A	S1						3.06	OK	-0.16	-1.35	8.50
	S2	2.89	OK	-0.32	-6.79	22.94	3.01	OK	-0.36	-3.05	8.65
	L										
3RD A	S1						5.41	OK	0.74	4.68	4.81
	S2	4.99	OK	-0.25	-3.47	13.72	5.28	OK	0.35	2.14	4.93
	L						10.55				
4TH A	S1	10.38					10.50	OK	0.40	1.30	2.47
	S2		OK	-0.05	-0.35	7.23		OK	0.32	0.81	2.48
	L										
5TH A	S1						30.17	warning	-1.49	-3.40	0.86
	S2	32.15	OK	0.76	2.92	3.15	30.90	OK	-0.48	-1.06	0.84
	L										
6TH a	S1						41.27	Action	-32.43	-20.71	0.63
	S2	55.42	Action	2.50	6.46	2.35	43.29	Action	-20.34	-16.84	0.60
	L										
5TH B	S1						30.48	Action	-2.88	-2.42	0.85
	S2	32.65	warning	1.34	4.53	3.16	31.18	OK	-0.16	-0.18	0.83
	L										
4TH B	S1						10.70	OK	0.79	2.76	2.43
	S2	10.82	OK	0.50	3.89	6.99	10.79	OK	1.00	3.62	2.41
	L										
3TH B	S1						5.49	OK	0.92	6.21	4.74
	S2	5.26	OK	0.12	1.82	13.01	5.43	OK	0.64	5.05	4.79
	L										
2ND B	S1						3.42	OK	0.85	10.23	7.61
	S2	3.13	OK	0.05	1.04	21.13	3.34	OK	0.62	7.59	7.79
	L										
1ST B	S1						1.50	warning	1.19	44.45	17.29
	S2	1.22	OK	0.25	17.28	52.47	1.42	OK	0.93	36.49	18.30

Table 8.II.a.- En value, bias and reported expanded uncertainty of the participants: toluene

Toluene		VMM-1					VMM-2					EKONERG				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	3.59	warning	-1.31	-24.23	15.27	2.99	Action	-2.45	-37.00	7.03					
1ST A	S1	4.35	OK	0.65	13.35	3.26	3.92	OK	0.09	2.14	12.24	3.57	OK	-0.32	-6.98	9.52
	S2	4.03	OK	0.39	5.02	3.52	3.50	OK	-0.71	-8.80	1.60	3.32	OK	-0.91	-13.49	9.64
	L	6.35	OK	-0.53	-39.82	122.81	5.50	OK	-0.55	-47.88	164.99					
2ND A	S1	9.96	OK	-0.56	-8.24	15.90	10.20	OK	-0.32	-6.03	20.24	8.76	Action	-2.89	-19.30	8.26
	S2	9.94	OK	-0.61	-8.47	14.66	10.29	OK	-0.24	-5.20	22.55	8.35	Action	-3.07	-23.07	8.31
	L	18.15	OK	0.43	2.69	2.03										
3RD A	S1	17.28	OK	-0.80	-4.49	4.91	19.78	Action	2.82	9.33	1.00	15.39	Action	-2.02	-14.93	7.89
	S2	18.05	OK	-0.05	-0.26	4.00	20.42	Action	3.86	12.87	0.41	15.64	Action	-1.79	-13.55	7.88
	L	36.64	OK	0.53	2.86	2.64										
4TH A	S1	37.73	OK	0.73	2.68	2.68	43.49	Action	5.76	15.77	1.10	31.47	Action	-1.94	-13.66	7.64
	S2	37.73	warning	1.18	3.51	2.21	43.49	Action	7.60	19.33	1.43	31.62	Action	-1.92	-13.24	7.64
	L	112.58	warning	1.26	5.39	2.82										
5TH A	S1	114.88	Action	5.02	5.07	0.75	129.16	Action	27.65	18.14	0.15	90.31	Action	-2.80	-17.40	7.48
	S2	116.10	Action	6.49	6.19	0.75	133.72	Action	12.32	22.31	1.42	91.40	Action	-2.61	-16.40	7.48
	L	192.89	warning	1.26	5.39	2.82										
6TH a	S1	196.73	Action	5.02	5.07	0.75	221.42	Action	27.65	18.14	0.15	119.78	Action	-2.80	-17.40	7.48
	S2	195.43	Action	6.49	6.19	0.75	232.15	Action	12.32	22.31	1.42	123.32	Action	-2.61	-16.40	7.48
	L	113.27	warning	1.34	6.57	2.47										
5TH B	S1	117.18	Action	3.81	7.18	0.71	132.40	Action	11.49	21.10	0.52	90.77	Action	-2.63	-16.98	7.48
	S2	117.13	Action	4.00	7.13	1.20	136.92	Action	16.34	25.23	0.73	91.78	Action	-2.51	-16.05	7.48
	L	37.18	OK	0.58	4.63	5.07										
4TH B	S1	38.72	warning	1.43	6.24	1.97	44.34	Action	5.09	21.64	1.56	31.97	Action	-1.59	-12.28	7.64
	S2	38.98	Action	1.86	6.95	1.23	45.84	Action	4.96	25.76	3.05	32.39	warning	-1.46	-11.13	7.63
	L	18.10	OK	0.41	2.99	3.30	20.16	Action	2.24	14.74	0.42					
3TH B	S1	18.94	OK	0.92	4.66	1.42	21.16	Action	3.16	16.93	1.94	15.86	warning	-1.46	-12.33	7.88
	S2	18.99	OK	0.95	4.97	1.79	21.88	Action	4.05	20.94	1.43	15.89	warning	-1.44	-12.17	7.87
	L															
2ND B	S1	11.27	OK	0.53	3.78	2.13	12.12	Action	1.73	11.66	0.23	9.47	warning	-1.30	-12.76	8.19
	S2	11.31	OK	0.63	4.20	0.00	12.48	Action	2.04	14.94	2.61	9.43	warning	-1.34	-13.12	8.21
	L															
1ST B	S1	4.57	OK	0.76	19.08	7.44	4.32	OK	0.42	12.44	15.39	3.74	OK	-0.10	-2.54	9.41
	S2	4.72	OK	0.83	22.87	9.88	4.45	OK	0.56	15.96	12.09	3.69	OK	-0.15	-3.84	9.43

Table 8,II,b.- E_n value, bias and reported expanded uncertainty of the participants: toluene

Toluene		HMS					EPA-1					EPA-2				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %		STATE	En	BIAS %	EU %
	L	3.35	Action	-1.87	-29.31	8.57	1.38	Action	-4.29	-70.90	27.56	0.86	Action	-5.36	-81.81	26.91
1ST A	S1	3.99	OK	0.19	4.07	7.51	3.29	OK	-0.46	-14.17	26.72	1.30	Action	-2.99	-66.07	27.04
	S2	3.65	OK	-0.35	-4.99	7.68										
	L															
2ND A	S1	9.84	Action	-1.95	-9.33	5.28	6.45	Action	-2.53	-40.54	26.96	2.91	Action	-10.10	-73.18	27.00
	S2	9.72	Action	-1.73	-10.47	5.15										
	L											11.13	Action	-2.06	-37.05	27.03
3RD A	S1	16.81	warning	-1.29	-7.07	4.88	11.66	Action	-2.02	-35.54	26.93	5.73	Action	-7.51	-68.35	27.00
	S2	16.78	warning	-1.29	-7.25	4.89										
	L	34.37	OK	-0.53	-3.49	4.74						35.60	OK	0.00	-0.05	27.09
4TH A	S1	34.13	warning	-1.26	-6.35	4.75	19.07	Action	-3.33	-47.67	26.95	12.12	Action	-7.18	-66.74	26.99
	S2	34.47	warning	-1.11	-5.41	4.76										
	L	102.53	OK	-0.73	-4.01	4.69						60.04	Action	-2.83	-43.79	27.01
5TH A	S1	102.05	Action	-1.51	-6.66	4.68	36.04	Action	-7.51	-67.04	27.03	38.30	Action	-6.85	-64.97	27.00
	S2	103.53	warning	-1.18	-5.30	4.69										
	L	164.84	OK	-0.73	-4.01	4.69						38.17	Action	-2.83	-43.79	27.01
6TH a	S1	164.84	Action	-1.51	-6.66	4.68		Action	-7.51	-67.04	27.03		Action	-6.85	-64.97	27.00
	S2	166.31	warning	-1.18	-5.30	4.69										
	L	103.32	OK	-0.45	-2.79	4.71						12.44	Action	-17.02	-88.30	27.00
5TH B	S1	102.99	warning	-1.22	-5.80	4.68										
	S2	104.32	OK	-0.99	-4.59	4.68										
	L	34.69	OK	-0.31	-2.37	4.76						5.94	Action	-11.16	-83.29	27.06
4TH B	S1	17.29	Action	-8.92	-52.57	9.49										
	S2	35.18	OK	-0.61	-3.49	4.72										
	L	17.05	OK	-0.36	-2.95	4.91										
3TH B	S1	17.29	OK	-0.66	-4.44	4.86										
	S2	17.19	OK	-0.87	-4.97	3.14										
	L															
2ND B	S1	10.27	OK	-0.65	-5.40	5.26										
	S2	10.35	OK	-0.39	-4.68	10.44										
	L															
1ST B	S1	4.03	OK	0.20	5.09	7.44										
	S2	4.05	OK	0.22	5.62	7.40										

Table 8.II.c.- En value, bias and reported expanded uncertainty of the participants: toluene

Toluene		AAA					GIOS					IPH_S				
			STATE	En	BIAS %	EU %		STATE	En	BIAS %	EU %		*STATE*	*En*	*BIAS %*	*EU %*
	L	4.48	OK	-0.37	-5.41	2.87	4.23	OK	-0.53	-10.68	15.60					
1ST A	S1	5.42			41.10		6.09	Action	1.84	58.66	15.60	*4.09*	*OK*	*0.13*	*6.52*	*43.74*
	S2	4.63			20.62		4.75	warning	1.04	23.75	15.58	*3.80*	*OK*	*-0.02*	*-1.11*	*44.64*
	L	9.64			-8.61											
2ND A	S1	9.85			-9.27		10.00	OK	-0.55	-7.91	15.61	*9.63*	*OK*	*-0.34*	*-11.26*	*36.98*
	S2	10.13			-6.68		9.33	warning	-1.01	-14.08	15.59	*9.49*	*OK*	*-0.39*	*-12.60*	*37.07*
	L															
3RD A	S1	18.41			1.74		17.92	OK	-0.06	-0.93	15.60	*16.81*	*OK*	*-0.22*	*-7.11*	*34.86*
	S2	18.93			4.66		17.37	OK	-0.26	-3.99	15.60	*16.82*	*OK*	*-0.22*	*-7.05*	*34.85*
	L						35.77	OK	0.03	0.43	15.68	*37.30*				
4TH A	S1	34.01			-6.70		36.94	OK	0.08	1.35	15.60	*35.08*	*OK*	*-0.12*	*-3.76*	*33.37*
	S2	35.37			-2.96		35.94	OK	-0.09	-1.38	15.60	*35.23*	*OK*	*-0.10*	*-3.33*	*33.36*
	L						103.87	OK	-0.18	-2.76	15.64					
5TH A	S1	76.67			-29.88		103.47	OK	-0.36	-5.36	15.60	*113.71*	*OK*	*0.12*	*4.00*	*32.42*
	S2	78.77			-27.96		102.34	OK	-0.44	-6.40	15.60	*115.08*	*OK*	*0.15*	*5.26*	*32.42*
	L						170.02	OK	-0.18	-2.76	15.64					
6TH a	S1	100.83			-29.88		169.55	OK	-0.36	-5.36	15.60	*195.15*	*OK*	*0.12*	*4.00*	*32.42*
	S2	104.40			-27.96		168.00	OK	-0.44	-6.40	15.60	*194.40*	*OK*	*0.15*	*5.26*	*32.42*
	L						106.83	OK	0.03	0.50	15.69					
5TH B	S1	77.56			-29.06		104.52	OK	-0.29	-4.40	15.60	*115.80*	*OK*	*0.17*	*5.92*	*32.41*
	S2	79.69			-27.11		106.11	OK	-0.19	-2.95	15.60	*115.56*	*OK*	*0.17*	*5.69*	*32.42*
	L						38.79	OK	0.49	9.16	16.15					
4TH B	S1	35.72			-1.99		39.79	OK	0.53	9.18	15.60	*35.95*	*OK*	*-0.04*	*-1.36*	*33.33*
	S2	36.77			0.90		39.66	OK	0.51	8.81	15.60	*36.08*	*OK*	*-0.03*	*-1.02*	*33.33*
	L						19.38	OK	0.56	10.30	15.68					
3TH B	S1	19.27			6.53		19.88	OK	0.55	9.87	15.60	*17.19*	*OK*	*-0.15*	*-4.98*	*34.80*
	S2						19.80	OK	0.53	9.45	15.60	*17.15*	*OK*	*-0.16*	*-5.18*	*34.80*
	L															
2ND B	S1	11.89			9.49		12.08	OK	0.61	11.33	15.61	*9.84*	*OK*	*-0.27*	*-9.33*	*36.88*
	S2						12.01	OK	0.57	10.62	15.61	*9.90*	*OK*	*-0.26*	*-8.79*	*36.85*
	L															
1ST B	S1	5.49			43.11		6.19	Action	1.77	61.17	15.59	*4.09*	*OK*	*0.13*	*6.65*	*43.73*
	S2	0.55			-85.72		6.21	Action	1.74	61.69	15.60	*4.14*	*OK*	*0.15*	*7.88*	*43.57*

Table 8.II.d.- En value, bias and reported expanded uncertainty of the participants toluene

Toluene		ISCIII					AEA				
			STATE	En	BIAS %	EU %		STATE	En	BIAS %	EU %
	L										
1ST A	S1						5.22	warning	1.34	36.05	13.14
	S2	4.71	OK	0.94	22.60	16.80	4.89	warning	1.26	27.40	14.03
	L										
2ND A	S1						10.58	OK	-0.40	-2.52	6.48
	S2	10.94	OK	0.08	0.77	9.25	11.22	OK	0.45	3.38	6.11
	L										
3RD A	S1						19.91	Action	2.04	10.02	3.45
	S2	18.41	OK	0.27	1.73	5.30	20.67	Action	2.83	14.23	3.32
	L										
4TH A	S1						38.04	warning	1.43	4.38	1.80
	S2	38.08	warning	1.16	4.49	3.24	41.16	Action	4.85	12.93	1.67
	L										
5TH A	S1						74.15	Action	-36.18	-32.18	0.93
	S2	117.75	Action	3.61	7.70	1.92	3.44	Action	-119.00	-96.85	19.92
	L										
6TH a	S1						79.08	Action	-36.18	-32.18	0.93
	S2	198.42	Action	3.61	7.70	1.92	95.49	Action	-119.00	-96.85	19.92
	L										
5TH B	S1						71.02	Action	-19.11	-35.04	0.97
	S2	122.12	Action	4.28	11.70	2.18	61.54	Action	-31.42	-43.71	1.11
	L										
4TH B	S1						41.38	Action	3.18	13.53	1.66
	S2	41.69			14.38		43.81	Action	5.09	20.21	1.57
	L										
3TH B	S1						21.81	Action	3.34	20.57	3.14
	S2	20.50	Action	1.75	13.34	5.15	22.32	Action	3.78	23.37	3.07
	L										
2ND B	S1						13.17	Action	2.31	21.36	5.21
	S2	12.58	warning	1.49	15.92	7.19	13.41	Action	2.57	23.59	5.11
	L										
1ST B	S1						5.95	Action	1.86	55.04	11.53
	S2	5.87	Action	1.58	53.02	14.81	6.04	Action	1.88	57.32	11.36

Table 8.III.a.- En value, bias and reported expanded uncertainty of the participants: ethyl-benzene

Ethyl-benzene		VMM-1					VMM-2					EKONERG				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.57	Action	-2.39	-38.53	10.58	0.18	Action	-5.20	-80.42	23.83					
1ST A	S1	0.74	OK	0.39	31.88	11.35	0.21	OK	-0.79	-62.57	13.33	0.60	OK	0.08	6.93	20.00
	S2	0.58			3.37		0.19	warning	-1.20	-67.03	52.97	0.51	OK	-0.16	-9.11	22.35
	L	1.02	OK	-0.79	-49.60	123.94	0.44	Action	-1.90	-78.15	186.36					
2ND A	S1	2.33	OK	0.14	15.21	91.07	0.94	Action	-4.42	-53.77	25.67	1.66	Action	-1.77	-17.92	11.93
	S2	1.64	warning	-1.50	-19.15	14.68	0.88	Action	-6.26	-56.73	17.83	1.59	Action	-2.00	-21.38	12.20
	L	3.52	OK	0.37	4.11	10.07										
3RD A	S1	2.96	warning	-1.32	-12.19	3.85	2.22			-34.14		3.14	OK	-0.55	-6.85	9.81
	S2	2.91	Action	-1.72	-13.82	1.45	2.18	Action	-4.24	-35.33	3.85	3.12	OK	-0.62	-7.44	9.81
	L	6.72	Action	-1.72	-4.27	1.58	5.88					6.27				
4TH A	S1	6.73	OK	-0.17	-1.05	3.36	5.93	Action	-2.44	-13.41	1.94	6.27	OK	-0.81	-7.67	8.58
	S2	6.51	OK	-0.22	-0.89	0.42		Action	-2.63	-12.67	2.87		OK	-0.86	-7.67	8.61
	L	19.70	warning	-1.00	-3.43	3.28										
5TH A	S1	20.04	OK	-0.96	-1.65	1.34	22.75	Action	6.57	11.68	1.24	18.64	warning	-1.18	-8.50	7.80
	S2	20.18	OK	-0.58	-0.96	1.33	23.40	Action	9.98	14.87	0.97	18.63	warning	-1.19	-8.55	7.80
	L	33.58	OK	0.09	0.48	1.06										
6TH a	S1	34.38	OK	0.50	1.72	0.08	41.26	Action	6.42	22.06	0.10	31.63	OK	-0.81	-6.42	7.64
	S2	34.45	OK	0.67	1.92	0.00	42.59	Action	8.24	25.99	1.03	31.75	OK	-0.79	-6.07	7.63
	L	20.26	OK	-0.04	-0.22	4.67										
5TH B	S1	20.58	OK	0.26	1.00	0.89	23.45	Action	3.98	15.09	0.55	18.95	OK	-0.85	-6.97	7.80
	S2	20.40	OK	0.04	0.12	1.87	24.13	Action	6.30	18.45	0.70	18.89	OK	-0.94	-7.27	7.80
	L	6.81	OK	0.05	0.25	3.66										
4TH B	S1	7.14	OK	0.68	5.14	1.99	6.33	OK	-0.93	-6.79	1.33	6.51	OK	-0.38	-4.14	8.57
	S2	7.21	OK	0.95	6.17	1.58	6.46	OK	-0.72	-4.95	2.85	6.47	OK	-0.46	-4.73	8.56
	L	3.00	Action	-2.14	-10.62	2.06	2.19	Action	-7.41	-34.75	1.28					
3TH B	S1	3.13	OK	-0.69	-7.29	1.34	2.47	Action	-2.55	-26.87	1.70	3.24	OK	-0.28	-3.88	9.69
	S2	3.09	OK	-0.76	-8.48	3.18	2.48	Action	-2.12	-26.57	8.57	3.22	OK	-0.31	-4.47	9.75
	L															
2ND B	S1	1.90	OK	-0.39	-6.30	2.22	1.20	Action	-2.53	-40.91	3.51	1.94	OK	-0.21	-4.08	11.24
	S2	1.89	OK	-0.42	-6.54	1.48	1.18	Action	-2.68	-41.90	1.19	1.92	OK	-0.27	-5.06	11.35
	L															
1ST B	S1	0.75	OK	0.46	32.77	17.18	0.27	OK	-0.76	-52.77	26.42	0.62	OK	0.15	10.49	19.68
	S2	0.75	OK	0.44	33.67	18.93	0.27	OK	-0.71	-51.88	20.74	0.62	OK	0.14	10.50	19.68

Table 8.III.b.- En value, bias and reported expanded uncertainty of the participants: ethyl-benzene

Ethyl-benzene		HMS					EPA-1					EPA-2				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.53	Action	-2.48	-42.08	14.39										
1ST A	S1	0.64	OK	0.18	14.24	11.86										
	S2	0.56	OK	0.00	-0.02	13.19										
	L															
2ND A	S1	1.81	Action	-1.71	-10.36	6.07										
	S2	1.77	Action	-1.71	-12.38	6.21										
	L															
3RD A	S1	3.03	warning	-1.02	-9.99	5.27										
	S2	3.02	warning	-1.14	-10.53	5.24										
	L	6.14	Action	-1.76	-8.71	4.98										
4TH A	S1	6.29	warning	-1.41	-9.66	4.89										
	S2	6.21	warning	-1.22	-7.34	4.77										
	L	18.63	Action	-1.92	-8.69	4.74										
5TH A	S1	18.52	Action	-2.04	-9.10	4.75										
	S2	18.72	Action	-1.83	-8.11	4.70										
	L	31.50	OK	-0.86	-5.75	4.70										
6TH a	S1	31.13	warning	-1.42	-7.90	4.75										
	S2	31.60	warning	-1.23	-6.51	4.75										
	L	18.85	warning	-1.42	-7.14	4.71										
5TH B	S1	18.77	warning	-1.37	-7.84	4.69										
	S2	18.97	warning	-1.32	-6.90	4.75										
	L	6.39	OK	-0.93	-5.85	5.28										
4TH B	S1	6.49	OK	-0.52	-4.45	4.93										
	S2	6.50	OK	-0.55	-4.31	4.92										
	L	3.07	warning	-1.27	-8.50	5.31										
3TH B	S1	3.14	OK	-0.59	-6.82	5.22										
	S2	3.15	OK	-0.56	-6.67	5.09										
	L															
2ND B	S1	1.91	OK	-0.32	-5.46	5.96										
	S2	1.92	OK	-0.32	-5.26	5.95										
	L															
1ST B	S1	0.66	OK	0.24	16.73	11.60										
	S2	0.66	OK	0.24	17.45	11.53										

Table 8.III.c.- En value, bias and reported expanded uncertainty of the participants: ethyl-benzene

Ethyl-benzene		AAA					GIOS					IPH_S				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L						0.89	OK	-0.13	-3.24	20.27					
1ST A	S1						0.95	OK	0.82	68.95	15.61	0.35	OK	-0.28	-37.62	169.14
	S2						0.55	OK	-0.03	-1.80	18.15	0.26	OK	-0.47	-53.31	215.27
	L															
2ND A	S1						1.79	OK	-0.84	-11.69	15.57	1.43	OK	-0.63	-29.34	65.64
	S2						1.48	Action	-2.19	-26.97	15.57	1.35	OK	-0.74	-33.44	67.61
	L															
3RD A	S1						3.35	OK	-0.03	-0.56	15.57	2.85	OK	-0.37	-15.54	48.89
	S2						3.22	OK	-0.27	-4.50	15.59	2.80	OK	-0.41	-16.93	49.14
	L						7.10	OK	0.11	1.77	15.63					
4TH A	S1						6.77	OK	0.27	4.55	15.61	6.54	OK	-0.06	-2.14	39.21
	S2						6.92	OK	-0.02	-0.32	15.60	6.94	OK	-0.10	-3.68	39.35
	L						19.32	OK	-0.36	-5.29	15.61					
5TH A	S1						18.81	OK	-0.53	-7.67	15.60	18.60	OK	-0.27	-8.69	34.58
	S2						18.48	OK	-0.66	-9.29	15.60	18.63	OK	-0.27	-8.57	34.58
	L						34.02	OK	0.11	1.81	15.62					
6TH a	S1						32.88	OK	-0.18	-2.73	15.60	32.94	OK	-0.08	-2.54	33.45
	S2						32.99	OK	-0.16	-2.41	15.60	32.78	OK	-0.09	-3.03	33.46
	L						20.34	OK	0.01	0.17	15.62					
5TH B	S1						20.04	OK	-0.10	-1.61	15.60	18.95	OK	-0.22	-6.99	34.54
	S2						19.91	OK	-0.15	-2.26	15.60	18.72	OK	-0.25	-8.09	34.57
	L						7.65	OK	0.68	12.72	16.18					
4TH B	S1						7.89	OK	0.83	16.24	15.61	6.77	OK	-0.01	-0.35	39.10
	S2						7.83	OK	0.80	15.27	15.61	6.63	OK	-0.06	-2.37	39.25
	L						3.84	OK	0.77	14.32	15.81					
3TH B	S1						3.88	OK	0.73	15.13	15.61	2.89	OK	-0.33	-14.27	48.58
	S2						3.84	OK	0.67	13.83	15.59	2.84	OK	-0.37	-15.89	48.96
	L															
2ND B	S1						2.25	OK	0.47	11.20	15.56	1.46	OK	-0.56	-27.91	64.88
	S2						2.16	OK	0.30	6.86	15.64	1.43	OK	-0.60	-29.19	65.50
	L															
1ST B	S1						0.90	OK	0.84	61.11	15.71	0.33	OK	-0.34	-41.72	178.59
	S2						0.90	OK	0.79	61.12	15.71	0.31	OK	-0.36	-45.64	189.51

Table 8.III.d.- En value, bias and reported expanded uncertainty of the participants: ethyl-benzene

Ethyl-benzene		ISCIII					AEA				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L										
1ST A	S1						1.45	OK	0.33	158.95	184.86
	S2						0.85	OK	0.11	50.96	317.12
	L										
2ND A	S1						2.36	OK	0.13	16.84	113.67
	S2	0.34			-83.43		2.18	OK	0.06	7.99	122.99
	L										
3RD A	S1						4.48	OK	0.41	32.87	59.97
	S2	2.47	OK	-0.99	-26.72	35.37	4.29	OK	0.34	27.18	62.65
	L						7.94				
4TH A	S1	7.22					7.97	OK	0.42	16.88	33.84
	S2		OK	0.44	6.38	13.11		OK	0.44	17.32	33.71
	L										
5TH A	S1						22.67	OK	0.85	11.30	11.85
	S2	20.75	OK	0.32	1.85	5.60	22.99	OK	0.97	12.86	11.68
	L										
6TH a	S1						37.99	warning	1.43	12.39	7.07
	S2	35.15	OK	0.79	3.98	3.96	39.15	Action	1.87	15.82	6.86
	L										
5TH B	S1						23.50	warning	1.12	15.36	11.43
	S2	21.81	warning	1.11	7.06	5.32	24.10	warning	1.36	18.30	11.15
	L										
4TH B	S1						8.73	OK	0.71	28.58	30.76
	S2	8.36	warning	1.45	23.03	11.87	8.68	OK	0.70	27.85	30.94
	L										
3TH B	S1						4.74	OK	0.51	40.68	56.64
	S2	3.28	OK	-0.09	-2.66	27.25	4.44	OK	0.39	31.63	60.54
	L										
2ND B	S1						2.84	OK	0.30	40.42	94.58
	S2	0.97			-51.89		2.89	OK	0.32	42.95	92.91
	L										
1ST B	S1						1.18	OK	0.23	110.47	227.43
	S2						1.22	OK	0.24	116.72	220.89

Table 8.IV.a.- En value, bias and reported expanded uncertainty of the participants: m,p-xylene

m,p-Xylene		VMM-1					VMM-2					EKONERG				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.76	OK	-0.47	-17.85	13.77	0.17	Action	-2.21	-81.32	39.18					
1ST A	S1	0.88	OK	0.25	39.27	3.18	0.30	OK	-0.33	-53.31	33.22	0.75	OK	0.12	18.70	17.33
	S2	0.66	OK	0.04	4.46	4.24	0.17	OK	-0.65	-73.89	8.48	0.64	OK	0.01	1.29	19.06
	L	1.09	OK	-0.55	-46.16	124.59	0.39	warning	-1.31	-80.74	188.72					
2ND A	S1	2.28	OK	0.10	7.91	76.93	0.90	Action	-5.06	-57.64	23.69	1.88	OK	-0.96	-11.02	11.38
	S2	1.61	warning	-1.20	-24.03	11.46	0.84	Action	-2.49	-60.24	40.48	1.76	OK	-0.81	-16.69	11.70
	L	4.04	OK	0.92	18.89	16.46										
3RD A	S1	2.95	warning	-1.01	-16.23	0.95	2.13	Action	-2.47	-39.66	0.66	3.65	OK	0.19	3.65	9.48
	S2	3.07	OK	-0.88	-12.96	5.09	2.09	Action	-2.88	-40.65	1.34	3.63	OK	0.18	3.08	9.48
	L	7.59	Action	2.08	8.39	2.26	5.67					7.33				
4TH A	S1	7.51	OK	0.88	6.91	2.79	5.75	Action	-2.73	-20.15	1.73	7.34	OK	0.29	3.32	8.43
	S2	7.41	OK	0.95	5.79	2.45		Action	-3.15	-18.95	2.96		OK	0.34	3.46	8.42
	L	21.67	Action	2.08	8.39	2.26										
5TH A	S1	22.52	OK	0.88	6.91	2.79	22.11	Action	-2.73	-20.15	1.73	21.67	OK	0.29	3.32	8.43
	S2	22.67	OK	0.95	5.79	2.45	22.73	Action	-3.15	-18.95	2.96	21.75	OK	0.34	3.46	8.42
	L	37.91	Action	1.85	13.41	0.60										
6TH a	S1	38.40	Action	11.99	8.42	0.52	39.95	Action	26.30	12.79	0.21	36.59	OK	0.42	3.31	7.60
	S2	38.52	Action	29.75	8.74	0.25	41.32	Action	9.06	16.66	1.57	37.76	OK	0.82	6.61	7.60
	L	22.17	OK	0.84	8.63	8.66										
5TH B	S1	23.19	Action	3.62	8.95	1.53	23.02	Action	4.43	8.17	0.24	22.09	OK	0.46	3.80	7.74
	S2	23.08	Action	3.35	8.45	1.84	23.60	Action	3.54	10.90	2.40	22.16	OK	0.50	4.13	7.73
	L	7.51	warning	1.12	9.98	6.39										
4TH B	S1	8.20	Action	1.67	15.51	0.85	6.32	warning	-1.15	-10.92	2.25	7.64	OK	0.60	7.69	8.38
	S2	8.16	warning	1.38	14.95	6.06	6.48	warning	-1.00	-8.66	2.62	7.63	OK	0.62	7.55	8.39
	L	3.12	warning	-1.08	-7.48	1.84	2.11	Action	-5.56	-37.47	1.33					
3TH B	S1	3.28	OK	-0.39	-7.00	2.14	2.41	Action	-1.75	-31.71	2.91	3.78	OK	0.36	7.34	9.42
	S2	3.18	OK	-0.52	-9.69	3.58	2.45	Action	-1.63	-30.43	5.80	3.79	OK	0.37	7.63	9.39
	L															
2ND B	S1	2.00	OK	-0.17	-5.34	0.00	1.14	warning	-1.45	-46.28	3.70	2.20	OK	0.12	4.13	10.82
	S2	1.96	OK	-0.23	-7.23	2.86	1.15	warning	-1.46	-45.57	4.87	2.22	OK	0.15	5.08	10.81
	L															
1ST B	S1	0.88	OK	0.29	38.48	17.83	0.29	OK	-0.42	-54.90	44.91	0.79	OK	0.19	25.03	16.96
	S2	0.88	OK	0.28	39.28	25.68	0.33	OK	-0.35	-47.77	25.45	0.77	OK	0.16	21.87	17.14

Table 8.IV.b.- En value, bias and reported expanded uncertainty of the participants: m,p-xylene

m,p-Xylene		HMS					EPA-1					EPA-2				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.78	OK	-0.40	-15.50	15.69										
1ST A	S1	0.79	OK	0.15	24.71	15.23										
	S2	0.67	OK	0.05	5.25	16.24										
	L															
2ND A	S1	1.83	warning	-1.07	-13.44	13.12										
	S2	1.75	OK	-0.80	-17.03	13.69										
	L															
3RD A	S1	3.02	OK	-0.72	-14.13	13.23										
	S2	2.97	OK	-0.88	-15.58	12.78										
	L	6.10	OK	-0.63	-8.03	13.48										
4TH A	S1	6.60	warning	-1.07	-14.07	12.80										
	S2	6.29	OK	-0.53	-6.94	12.72										
	L	19.91	OK	-0.63	-8.03	13.48										
5TH A	S1	19.74	warning	-1.07	-14.07	12.80										
	S2	19.95	OK	-0.53	-6.94	12.72										
	L	33.48	OK	0.01	0.16	12.78										
6TH a	S1	33.09	OK	-0.55	-6.58	12.81										
	S2	33.45	OK	-0.46	-5.56	12.79										
	L	20.14	OK	-0.10	-1.32	12.78										
5TH B	S1	20.06	OK	-0.47	-5.75	12.76										
	S2	20.22	OK	-0.41	-4.99	12.76										
	L	6.97	OK	0.15	2.15	13.29										
4TH B	S1	6.88	OK	-0.20	-3.04	12.79										
	S2	6.84	OK	-0.24	-3.64	12.87										
	L	3.06	OK	-0.67	-9.17	13.12										
3TH B	S1	3.15	OK	-0.49	-10.52	12.69										
	S2	3.12	OK	-0.53	-11.48	12.83										
	L															
2ND B	S1	1.93	OK	-0.25	-8.61	13.46										
	S2	1.90	OK	-0.30	-9.97	13.67										
	L															
1ST B	S1	0.79	OK	0.19	24.71	15.23										
	S2	0.76	OK	0.15	20.60	15.49										

Table 8.IV.c.- En value, bias and reported expanded uncertainty of the participants: m,p-xylene

m,p-Xylene		AAA					GIOS					IPH_S				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L						1.90	Action	1.71	106.33	24.51					
1ST A	S1						1.41	OK	0.76	123.31	15.59	0.48	OK	-0.13	-24.35	132.22
	S2						0.75	OK	0.16	18.70	15.47	0.25	OK	-0.42	-60.75	225.81
	L															
2ND A	S1						2.05	OK	-0.18	-2.93	15.60	1.32	OK	-0.87	-37.34	68.28
	S2						1.54	warning	-1.26	-26.97	15.55	1.05	warning	-1.18	-50.44	77.94
	L															
3RD A	S1						3.55	OK	0.04	0.81	12.79	2.61	OK	-0.64	-26.00	50.42
	S2						3.29	OK	-0.33	-6.72	15.59	2.47	OK	-0.77	-29.92	51.46
	L						7.10	OK	0.38	6.39	15.62					
4TH A	S1						6.70	OK	0.00	0.08	15.61	6.13	OK	-0.33	-11.72	39.66
	S2						7.28	OK	-0.35	-5.51	15.60	7.06	OK	-0.39	-13.61	39.84
	L						19.98	OK	0.38	6.39	15.62					
5TH A	S1						19.03	OK	0.00	0.08	15.61	17.88	OK	-0.33	-11.72	39.66
	S2						18.92	OK	-0.35	-5.51	15.60	18.35	OK	-0.39	-13.61	39.84
	L						35.35	OK	0.32	5.76	15.63					
6TH a	S1						33.60	OK	-0.35	-5.12	15.60	33.06	OK	-0.21	-6.65	33.45
	S2						33.80	OK	-0.31	-4.56	15.60	33.23	OK	-0.20	-6.17	33.45
	L						21.29	OK	0.14	4.28	28.33					
5TH B	S1						20.77	OK	-0.16	-2.40	15.60	18.54	OK	-0.43	-12.90	34.59
	S2						20.75	OK	-0.16	-2.50	15.60	18.52	OK	-0.43	-12.97	34.59
	L						8.07	OK	0.90	18.27	16.44					
4TH B	S1						8.29	OK	0.82	16.87	15.61	6.25	OK	-0.33	-11.86	39.66
	S2						8.14	OK	0.74	14.68	15.61	6.29	OK	-0.31	-11.37	39.63
	L						4.19	warning	1.14	24.16	16.20					
3TH B	S1						4.30	OK	0.84	22.11	15.58	2.56	OK	-0.66	-27.22	50.72
	S2						4.15	OK	0.68	17.71	15.59	2.51	OK	-0.71	-28.75	51.10
	L															
2ND B	S1						2.49	OK	0.49	17.95	15.57	1.28	OK	-0.75	-39.42	69.53
	S2						2.36	OK	0.33	11.66	15.60	1.13	OK	-0.92	-46.61	74.47
	L															
1ST B	S1						1.24	OK	0.72	95.45	15.55	0.33	OK	-0.30	-48.09	178.05
	S2						1.17	OK	0.61	85.02	15.57	0.33	OK	-0.29	-47.61	177.04

Table 8.IV.d.- En value, bias and reported expanded uncertainty of the participants: m,p-xylene

m,p-Xylene		ISCIII					AEA				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L										
1ST A	S1						3.21	OK	0.37	408.65	217.55
	S2						1.05	OK	0.06	65.55	668.45
	L										
2ND A	S1						2.91	OK	0.11	37.73	240.27
	S2	0.07			-96.54		2.19	OK	0.01	3.80	318.83
	L										
3RD A	S1						4.84	OK	0.19	37.55	144.34
	S2	1.05	Action	-2.56	-70.30	79.43	4.41	OK	0.13	25.26	158.51
	L						8.19				
4TH A	S1	3.32					7.99	OK	0.16	15.46	85.36
	S2		Action	-3.97	-53.22	26.14		OK	0.13	12.67	87.48
	L										
5TH A	S1						22.45	OK	0.16	15.46	85.36
	S2	10.09	Action	-3.97	-53.22	26.14	22.57	OK	0.13	12.67	87.48
	L										
6TH a	S1						36.41	OK	0.14	2.80	19.20
	S2	17.46	Action	-15.52	-50.72	6.63	37.81	OK	0.34	6.74	18.49
	L										
5TH B	S1						23.60	OK	0.33	10.91	29.62
	S2	10.75	Action	-10.03	-49.47	9.27	23.92	OK	0.38	12.42	29.23
	L										
4TH B	S1						8.98	OK	0.27	26.61	77.84
	S2	3.99	Action	-2.91	-43.80	22.34	9.11	OK	0.29	28.35	76.78
	L										
3TH B	S1						4.94	OK	0.20	40.28	141.54
	S2	1.53	Action	-1.89	-56.66	54.78	4.62	OK	0.16	31.11	151.44
	L										
2ND B	S1						3.00	OK	0.13	41.94	233.14
	S2	0.39			-81.73		3.10	OK	0.14	46.54	225.84
	L										
1ST B	S1						1.44	OK	0.11	127.58	486.23
	S2						1.48	OK	0.12	134.08	472.75

Table 8.V.a.- En value, bias and reported expanded uncertainty of the participants: o-xylene

o-Xylene		VMM-1					VMM-2					EKONERG				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.64	OK	0.19	16.91	15.81	0.17	OK	-0.77	-68.34	22.23					
1ST A	S1	0.88	OK	0.32	27.56	19.32	0.31	OK	-0.67	-55.79	13.77	0.69	OK	0.00	0.02	18.26
	S2	0.70	OK	0.01	0.75	6.04	0.21	warning	-1.08	-70.28	34.15	0.61	OK	-0.17	-11.57	19.67
	L	1.07	OK	-0.65	-47.43	132.15	0.42	Action	-1.68	-79.61	207.71					
2ND A	S1	1.83	warning	-1.49	-17.59	13.15	0.88	Action	-5.66	-60.49	24.23	1.67	Action	-2.43	-24.59	11.86
	S2	1.78	warning	-1.39	-19.84	16.68	0.79	Action	-5.13	-64.32	32.15	1.55	Action	-3.01	-30.00	12.26
	L	3.59	OK	0.33	5.22	10.25										
3RD A	S1	3.34	OK	-0.64	-9.51	9.34	2.05	Action	-3.68	-44.60	0.68	2.98	warning	-1.33	-19.26	9.93
	S2	3.32	warning	-1.04	-10.05	2.53	2.05	Action	-4.57	-44.59	4.79	2.94	Action	-1.66	-20.35	9.93
	L	7.11	OK	-0.16	-1.44	3.89	5.55					6.04				
4TH A	S1	7.00	OK	-0.84	-4.38	2.00	5.61	Action	-4.75	-25.36	3.06	6.00	Action	-2.20	-18.77	8.64
	S2	6.78	warning	-1.02	-5.93	5.06			-7.31	-24.55			Action	-2.49	-19.31	8.67
	L	20.54	OK	-0.04	-0.37	5.44										
5TH A	S1	20.32	OK	-0.57	-8.92	17.34	22.23	OK	-0.33	-0.34	1.02	17.93	Action	-3.12	-19.62	7.82
	S2	21.50	Action	-3.38	-3.63	1.12	22.64	Action	3.36	1.48	0.43	17.85	Action	-3.19	-19.98	7.82
	L	35.72	OK	0.66	9.10	1.71										
6TH a	S1	36.58	Action	-7.43	-3.00	0.19	40.45	Action	16.40	7.26	0.24	30.49	Action	-3.09	-19.14	7.65
	S2	36.55	Action	-3.02	-3.08	0.19	41.26	Action	9.22	9.41	0.17	31.43	Action	-2.58	-16.65	7.64
	L	20.85	OK	0.16	1.60	5.20										
5TH B	S1	22.02	OK	-0.46	-1.30	1.09	23.10	warning	1.31	3.56	0.61	18.25	Action	-2.63	-18.18	7.81
	S2	21.84	OK	-0.90	-2.09	1.56	23.30	Action	2.38	4.46	0.61	18.24	Action	-2.75	-18.23	7.81
	L	7.03	OK	0.23	2.53	4.26										
4TH B	S1	7.67	OK	0.39	3.15	4.43	6.08	Action	-2.59	-18.23	2.80	6.29	Action	-1.56	-15.41	8.59
	S2	7.39	OK	-0.11	-0.68	2.11	6.10	Action	-3.07	-18.03	1.15	6.34	Action	-1.58	-14.74	8.58
	L	3.48	OK	0.20	2.55	2.78	2.06	Action	-3.15	-39.41	4.77					
3TH B	S1	3.63	OK	-0.14	-1.79	4.30	2.34	Action	-2.95	-36.60	6.07	3.13	warning	-1.05	-15.20	9.78
	S2	3.75	OK	0.13	1.47	1.87	2.28	Action	-3.37	-38.36	5.63	3.06	warning	-1.26	-17.09	9.87
	L															
2ND B	S1	2.20	OK	-0.05	-0.88	0.64	1.08	Action	-2.76	-51.23	0.00	1.84	OK	-0.81	-16.91	11.52
	S2	2.21	OK	-0.02	-0.42	0.63	1.06	Action	-2.77	-52.13	5.28	1.84	OK	-0.81	-16.91	11.52
	L															
1ST B	S1	0.90	OK	0.36	30.46	12.67	0.32	OK	-0.65	-54.34	31.11	0.75	OK	0.10	8.72	17.33
	S2	0.96	OK	0.44	38.44	16.34	0.30	OK	-0.68	-57.23	14.24	0.75	OK	0.10	8.73	17.33

Table 8.V.b.- En value, bias and reported expanded uncertainty of the participants: o-xylene

o-Xylene		HMS					EPA-1					EPA-2				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L	0.62	OK	0.15	13.62	15.09										
1ST A	S1	0.75	OK	0.10	8.43	13.10										
	S2	0.66	OK	-0.07	-4.90	13.72										
	L															
2ND A	S1	1.88	warning	-1.38	-15.20	11.71										
	S2	1.81	Action	-1.78	-18.40	11.07										
	L															
3RD A	S1	3.15	OK	-0.97	-14.74	10.80										
	S2	3.15	warning	-1.11	-14.60	10.79										
	L	6.39	OK	-0.54	-7.05	10.96										
4TH A	S1	6.41	warning	-1.34	-14.13	10.96										
	S2	6.39	warning	-1.38	-13.78	10.92										
	L	19.05	OK	-0.61	-7.63	11.00										
5TH A	S1	18.91	Action	-1.63	-15.24	11.00										
	S2	19.14	Action	-1.51	-14.18	10.97										
	L	32.02	OK	-0.13	-2.18	10.95										
6TH a	S1	31.68	Action	-1.73	-15.99	10.99										
	S2	32.30	Action	-1.52	-14.35	10.96										
	L	19.31	OK	-0.44	-5.89	10.98										
5TH B	S1	19.23	warning	-1.41	-13.80	10.92										
	S2	19.43	warning	-1.32	-12.87	11.01										
	L	6.55	OK	-0.31	-4.50	11.05										
4TH B	S1	6.60	OK	-0.95	-11.19	10.90										
	S2	6.64	OK	-0.95	-10.73	10.85										
	L	3.25	OK	-0.25	-4.06	11.11										
3TH B	S1	3.32	OK	-0.66	-10.05	10.84										
	S2	3.32	OK	-0.69	-10.05	10.84										
	L															
2ND B	S1	1.99	OK	-0.49	-10.23	11.07										
	S2	1.98	OK	-0.51	-10.81	11.14										
	L															
1ST B	S1	0.78	OK	0.15	12.78	13.11										
	S2	0.78	OK	0.15	12.78	13.11										

Table 8.V.c.- En value, bias and reported expanded uncertainty of the participants o-xylene

o-Xylene		AAA					GIOS					IPH_S				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L						0.72	OK	0.34	31.58	21.21					
1ST A	S1						0.86	OK	0.29	24.66	15.58	0.46	OK	-0.27	-33.17	136.23
	S2						0.53	OK	-0.35	-23.31	18.90	0.38	OK	-0.41	-44.48	157.18
	L															
2ND A	S1						1.57	Action	-2.44	-29.29	15.58	1.51	OK	-0.73	-31.95	63.84
	S2						1.21	Action	-4.54	-45.22	15.66	1.37	OK	-0.91	-38.18	67.06
	L															
3RD A	S1						3.07	OK	-0.96	-16.96	15.60	2.98	OK	-0.47	-19.16	48.12
	S2						2.89	warning	-1.41	-21.73	15.58	2.99	OK	-0.48	-19.05	48.06
	L						6.88	OK	-0.04	-0.69	15.65					
4TH A	S1						6.64	OK	-0.49	-7.48	15.61	7.36	OK	0.06	2.46	38.30
	S2						6.83	OK	-0.75	-10.74	15.61	7.43	OK	-0.03	-0.99	38.52
	L						19.82	OK	-0.23	-3.90	15.76					
5TH A	S1						19.45	OK	-0.94	-12.81	15.60	22.40	OK	0.01	0.41	34.15
	S2						19.27	warning	-1.01	-13.60	15.60	22.44	OK	0.02	0.62	34.14
	L						34.68	OK	0.28	5.93	15.63					
6TH a	S1						33.76	OK	-0.75	-10.47	15.60	36.51	OK	-0.10	-3.17	33.32
	S2						33.52	OK	-0.80	-11.11	15.60	35.73	OK	-0.17	-5.23	33.35
	L						21.11	OK	0.16	2.88	15.66					
5TH B	S1						21.04	OK	-0.38	-5.69	15.60	22.81	OK	0.06	2.25	34.10
	S2						20.79	OK	-0.46	-6.78	15.60	22.59	OK	0.04	1.28	34.13
	L						7.79	OK	0.63	13.58	16.65					
4TH B	S1						8.11	OK	0.50	9.12	15.60	7.66	OK	0.07	2.96	38.27
	S2						8.05	OK	0.46	8.23	15.61	7.54	OK	0.03	1.37	38.37
	L						3.61	OK	0.31	6.39	15.74					
3TH B	S1						3.75	OK	0.08	1.57	15.58	3.08	OK	-0.40	-16.45	47.54
	S2						3.68	OK	-0.01	-0.24	15.59	3.06	OK	-0.42	-17.20	47.71
	L															
2ND B	S1						2.03	OK	-0.36	-8.38	15.57	1.55	OK	-0.63	-29.96	62.93
	S2						1.94	OK	-0.54	-12.39	15.57	1.50	OK	-0.69	-32.49	64.08
	L															
1ST B	S1						0.84	OK	0.25	21.48	15.51	0.42	OK	-0.33	-39.70	147.60
	S2						0.90	OK	0.36	31.05	15.71	0.39	OK	-0.36	-43.17	154.59

Table 8.V.d.- En value, bias and reported expanded uncertainty of the participants: o-xylene

o-Xylene		ISCIII					AEA				
		Mean	STATE	En	BIAS %	EU %	Mean	STATE	En	BIAS %	EU %
	L										
1ST A	S1						1.50	OK	0.43	117.44	120.13
	S2						0.95	OK	0.14	38.01	189.29
	L										
2ND A	S1						2.35	OK	0.07	5.89	76.84
	S2	0.03			-98.69		2.14	OK	-0.04	-3.36	84.21
	L										
3RD A	S1						4.17	OK	0.26	13.09	43.17
	S2	2.10	Action	-2.25	-43.24	29.60	4.04	OK	0.19	9.37	44.64
	L						8.15				
4TH A	S1	7.34					8.16	OK	0.39	9.56	22.12
	S2		OK	-0.14	-1.34	9.17		OK	0.40	9.69	22.09
	L										
5TH A	S1						23.61	OK	0.73	5.87	7.63
	S2	22.73	OK	0.51	1.91	3.65	24.04	OK	0.96	7.79	7.49
	L										
6TH a	S1						39.84	warning	1.18	5.67	4.52
	S2	37.77	OK	0.05	0.15	2.62	41.38	Action	1.99	9.73	4.36
	L										
5TH B	S1						25.37	Action	1.62	13.74	7.10
	S2	23.92	Action	1.71	7.24	3.59	25.91	Action	1.96	16.18	6.95
	L										
4TH B	S1						9.31	warning	1.00	25.20	19.36
	S2	8.77	warning	1.49	18.00	8.98	9.35	warning	1.03	25.73	19.27
	L										
3TH B	S1						4.73	OK	0.56	28.20	38.08
	S2	3.01	OK	-0.88	-18.34	21.78	4.71	OK	0.55	27.53	38.28
	L										
2ND B	S1						2.87	OK	0.35	29.60	62.79
	S2	0.64			-71.10		2.87	OK	0.36	29.79	62.70
	L										
1ST B	S1						1.39	OK	0.37	102.07	129.27
	S2						1.42	OK	0.39	106.14	126.72

Conclusions

The benzene reproducibility standard deviation of the exercise at 5 µg/m^3 was of circa 7.4 %.This value represents an improvement with respect to the last two inter-laboratory exercises in which the corresponding reproducibility were circa 12.5 %. Similarly, the average reproducibility and repeatability standard deviation of the exercise for benzene: 7.9 % and 4.7 %, respectively, fulfill the criteria for analytical robustness. Behind this improvement, it is noted that all laboratories were using certified reference standards for calibration and the standard deviation associated with each reported concentration was the result of the estimation of the associated analytical uncertainty.

With the exception of toluene, reproducibility values were consistent with that expected from the standard deviation defined by N37 for proficiency assessment. The high values of toluene reproducibility were probably due to an inappropriate operating calibration range for this compound.

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The excellent administrative support of Ms. Elisa Battistoni and the dedication of Mr. Luca Spano to the website during the preparation and execution of the inter-laboratory exercise have been greatly appreciated.

References

AQUILA N37: 2008. Protocol for inter-laboratory comparison exercise. Organization of inter-laboratory comparison exercises for gaseous air pollutants for EU National Air Quality Reference Laboratories and laboratories of the WHO Euro Region. [*http://ies.jrc.ec.europa.eu/aquila-project/role-and-tasks-of-national-reference-laboratories.html*](http://ies.jrc.ec.europa.eu/aquila-project/role-and-tasks-of-national-reference-laboratories.html)*.*

EC directive 2008/50/EC of the European Parliament of hte Council of 21 May 2008 on ambient air quality and cleaner air for Europe. OJ L152/1 of 11.6.2008.

ENV 13005 1999. Guide to the Expression of Uncertainty in Measurement.

EN14662-3: 2004. Ambient Air Quality - Standard method for the measurement of benzene concentrations - Part 3: Automated pumped sampling with in situ gas chromatography.

EUR 22523 EN. P. Pérez Ballesta, R. A. Field, R. Connolly, F. Lagler, I. Nikolova, N. Cao. "First EC-JRC aromatic (BTEX) compounds inter-laboratory comparison with automatic analysers".

EUR 23792 EN. P. Pérez Ballesta, R. Connolly, N. Cao, F. Lagler, M. Kapus Dukaric. Second EC-JRC aromatic compunds intercomparison with automatic analysers.

P. Pérez Ballesta, R. A. Field, E. De Saeger. Inter-laboratory exercises for volatile organic compound determination. Atmospheric Environment. 35, 5729-5740 (2001).

ISO GUM, 1993. Guide to the Expression of Uncertainty in Measurement.

ISO 5725-1: 1994. Accuracy (trueness and precision) of measurement methods and results. Part 1. General principles and definition.

ISO 5725-2: 1994. Accuracy (trueness and precision) of measurement methods and results. Part 2. Basic method for the determination of repeatability and reproducibility of a standard measurement method.

ISO 6143 : 1999. Gas analysis – Determination of the composition of calibration gas mixtures – Comparison methods.

ISO 13528: 2005. Statistical methods for use in proficiency testing by inter-laboratory comparison.

Annex

Third EC-JRC aromatic compounds inter-laboratory comparison with automatic analysers

Working Schedule for the inter-laboratory comparison exercise

Indicators of Mandel's statistic

Robust Analysis: Estimation of robust values of the average and standard deviation of a number of inter-laboratory measurements

Average repeatability, reproducibility and gamma values of the 2nd inter-laboratory exercise

Conversion factors for data reporting

Analysers and method description from participating laboratories

Working schedule for the inter-laboratory comparison exercise

Nov. 12th: Arrival of participants and installation of equipment: 14:00 to 17:30

Nov. 13th : Calibration: 9:00 – 13:30 / Synchronization: 13:30 / Measurements starting: 14:30

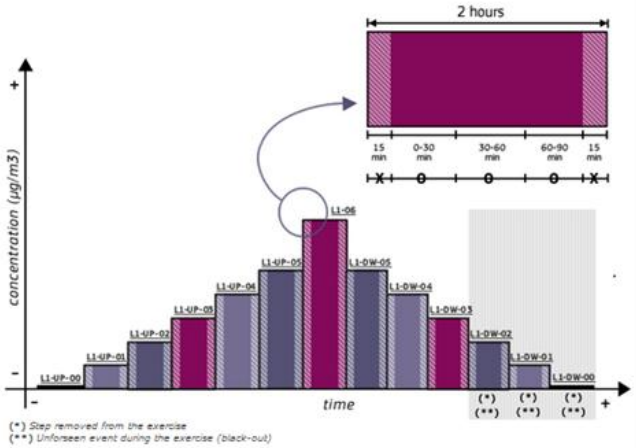
Nov. 14th : End of measurements: 15:30 / Calibration 15:30 – 17:30

Nov.15th : Dismantling of equipment and departure of participants

L1 - Long series

Started on Wednesday, 13 November at 14:30

At least three concentration analysis per level. The first and the last 15 minutes of each batch will not be considered as a valid measurement.



(*) Step removed from the exercise
(**) Unforseen event during the exercise (black-out)

Step name	Change in concentration	Reporting period	
L1-UP-00	0 µg/m3	14:30 - 15:00	13/11
		15:00 - 15:30	
		15:30 - 16:00	
L1-UP-01	1 µg/m3	16:30- 17:00	
		17:00 - 17:30	
		17:30 - 18:00	
L1-UP-02	3 µg/m3	18:30- 19:00	
		19:00 - 19:30	
		19:30 - 20:00	
L1-UP-03	5 µg/m3	20:30- 21:00	
		21:00 - 21:30	
		21:30 - 22:00	
L1-UP-04	10 µg/m3	22:30- 23:00	
		23:00 - 23:30	
		23:30 - 00:00	
L1-UP-05	30 µg/m3	00:30- 01:00	14/11
		01:00 - 01:30	
		01:30 - 02:00	
L1-06	50 µg/m3	02:30- 03:00	
		03:00 - 03:30	
		03:30 - 04:00	

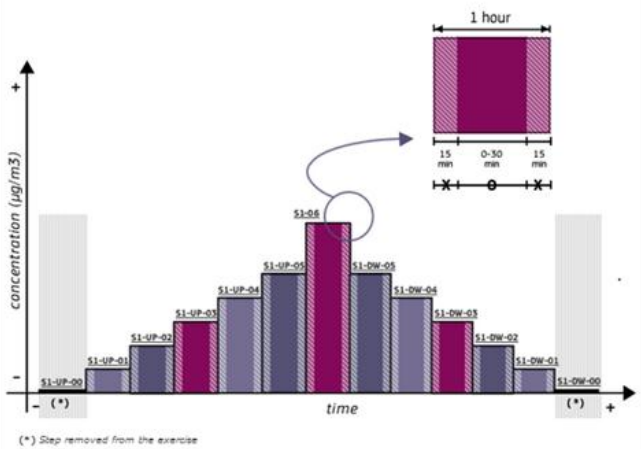
Blackout

Step name	Change in concentration	Reporting period	
L1-DW-05	30 µg/m3	04:30- 05:00	14/11
		05:00 - 05:30	
		05:30 - 06:00	
L1-DW-04	10 µg/m3	06:30- 07:00	
		07:00 - 07:30	
		07:30 - 08:00	
L1-DW-03	5 µg/m3	08:30- 09:00	
		09:00 - 09:30	
		09:30 - 10:00	

S1 - Short series

Started on Thursday, 14 November at 11:00

One concentration analysis per level. The first and the last 15 minutes of each batch will not be considered as a valid measurement



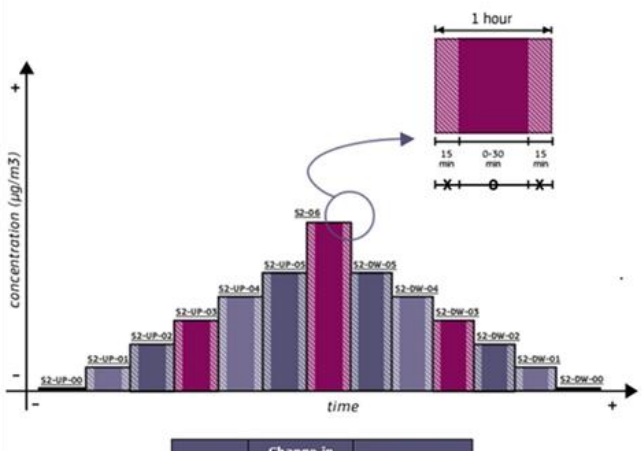
(*) Step removed from the exercise

Step name	Change in concentration	Reporting period	
S1-UP-01	1 µg/m3	11:00 - 11:30	14/11
S1-UP-02	3 µg/m3	12:00 - 12:30	
S1-UP-03	5 µg/m3	13:00 - 13:30	
S1-UP-04	10 µg/m3	14:00 - 14:30	
S1-UP-05	30 µg/m3	15:00 - 15:30	
S1-06	50 µg/m3	16:00 - 16:30	
S1-DW-05	30 µg/m3	17:00 - 17:30	
S1-DW-04	10 µg/m3	18:00 - 18:30	
S1-DW-03	5 µg/m3	19:00 - 19:30	
S1-DW-02	3 µg/m3	20:00 - 20:30	
S1-DW-01	1 µg/m3	21:00 - 21:30	

S2 - Short series

Started on Thursday, 14 November at 22:00

One concentration analysis per level. The first and the last 15 minutes of each batch will not be considered as a valid measurement



Step name	Change in concentration	Reporting period	
S2-UP-00	0 µg/m3	22:00 - 22:30	14/11
S2-UP-01	1 µg/m3	23:00 - 23:30	
S2-UP-02	3 µg/m3	00:00 - 00:30	15/11
S2-UP-03	5 µg/m3	01:00 - 01:30	
S2-UP-04	10 µg/m3	02:00 - 02:30	
S2-UP-05	30 µg/m3	03:00 - 03:30	
S2-06	50 µg/m3	04:00 - 04:30	
S2-DW-05	30 µg/m3	05:00 - 05:30	
S2-DW-04	10 µg/m3	06:00 - 06:30	
S2-DW-03	5 µg/m3	07:00 - 07:30	
S2-DW-02	3 µg/m3	08:00 - 08:30	
S2-DW-01	1 µg/m3	09:00 - 09:30	
S2-DW-00	0 µg/m3	10:00 - 10:30	

Indicators of Mandel's statistic

Number of	k values at* of s.l.		h values at s.l.	
Laboratories, p	1 %	5 % **	1 %	5 % **
3	1.53	1.40	1.15	1.15
4	1.60	1.44	1.49	1.42
5	1.65	1.46	1.72	1.57
6	1.68	1.48	1.87	1.66
7	1.70	1.49	1.98	1.71
8	1.71	1.50	2.06	1.75
9	1.73	1.50	2.13	1.78
10	1.74	1.50	2.18	1.80
11	1.74	1.51	2.22	1.82
12	1.75	1.51	2.25	1.83
13	1.76	1.51	2.27	1.84
14	1.76	1.52	2.30	1.85
15	1.76	1.52	2.32	1.86
16	1.77	1.52	2.33	1.86
17	1.77	1.52	2.35	1.87
18	1.77	1.52	2.36	1.88
19	1.78	1.52	2.37	1.88
20	1.78	1.52	2.39	1.89
21	1.78	1.52	2.39	1.89
22	1.78	1.52	2.40	1.89
23	1.78	1.53	2.41	1.90
24	1.79	1.53	2.42	1.90
25	1.79	1.53	2.42	1.90
26	1.79	1.53	2.43	1.90
27	1.79	1.53	2.44	1.91

* for 5 replicated values. ** s.l. : significance level

Robust Analysis: Estimation of robust values of the average and standard deviation of a number of inter-laboratory measurements

The robust estimation of an average value, $\overline{C}_i^*$, and standard deviation, s^*, of *p* inter-laboratory measurements is derived from a convergence process of the following equation:

$$\overline{C}_i^* = \frac{\sum C_i^*}{p}$$

$$s^* = 1.134 \cdot \sqrt{\frac{\sum (C_i - \overline{C}_i^*)^2}{(p-1)}}$$

Where recurrent values are calculated from these equations:

$$C_i^* = \begin{cases} \overline{C}_i^* - 1.5 \cdot s^* & \text{if} \quad C_i < \overline{C}_i^* - 1.5 \cdot s^* \\ \overline{C}_i^* + 1.5 \cdot s^* & \text{if} \quad C_i > \overline{C}_i^* + 1.5 \cdot s^* \\ C_i & \text{otherwise} \end{cases}$$

The initial values are calculated as:

$$\overline{C}_i^* = \text{median of } C_i \ (\text{i} = 1, 2, ...\text{p})$$

$$s^* = 1.483 \cdot \text{median of } \left| C_i - \overline{C}_i^* \right| (\text{i} = 1, 2, ...\text{p})$$

Average repeatability, reproducibility and gamma values of 2nd inter-laboratory exercise

	Repeatability, %	Reproducibility, %	Robustness (γ)
Benzene	1.4	17.8	17.2
Toluene	1.8	10.0	7.1
Ethyl-benzene	2.2	9.7	6.1
m,p-Xylene	4.2	8.0	2.1
o-Xylene	3.1	16.5	6.7

(EUR 23792EN 2009)

Conversion factors for data reporting

	Conversion factor µg/m^3 / ppb (v/v)
Benzene	1.4
Toluene	1.8
Ethyl-benzene	2.2
m,p-Xylene	4.2
o-Xylene	3.1

- *ppb(m/m) to ppb(v/v) factors were not taken into account.*

Analysers and method description from participating laboratories

VMM1
VMM2
EKONERG
HMS
EPA1
EPA2
AAA
GIOS
IPH_S
ISCIII
AEA

VMM1

Participating Laboratory	Vlaamse milieumaatschappij
Acronym	VMM-1

Characteristic of your BTEX analyser

Trademark	Chromatotec group
Model:	Airmobtx 1000, GC 866
Version:	GC 866
Year of manufacture:	2011

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:			X		
Other gases used:					X

Operating system:	windows embedded		
Cycle time, min:	15		
Adsorbent material:	carbotrap B		
Sampling control	pump+critical orifice		
Sampling temperature, °C	ambient		
Sample volume, ml	460 ml		
Number of adsorbent tubes	1		
Desorption temperature, `	380°C		
Desorption time, sec	120 sec		
Desorption flow, ml/min	3-4 ml/min		
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column			
Analytical column	metallic column (MXT 30CE)		
phase:			
length, m:	30 m		
diameter (ID) mm:	0,28 mm		
thickness (µm):	1 µm		
analytical conditions:	43°C (2°/min) -> 45°C (10°/min) -> 75°C (15°/min) ->165°C (120s)		

Traceability of your calibration Standard

Certified reference material (CRM):			
Certified by	Grace Davison Discovery Sciences		
Certified number:			
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)	
Benzene	11.33 ng/min	1.26 ng/min	k=3
Toluene	10.64 ng/min	1.42 ng/min	k=3
Ethyl-benzene	6.42 ng/min	1.12 ng/min	k=3
m-Xylene	8.63 ng/min	1.43 ng/min	k=3
p-Xylene	8.63 ng/min	1.43 ng/min	k=3
o-Xylene	17.34 ng/min	2.13 ng/min	k=3
Other methods			
Dilution of CRM			
Static Injection			
Permeation	portable permeation device, dilution possible between 600 and 2000 ml/min		
Additional comments			

VMM2

Participating Laboratory	Vlaamse milieumaatschappij					
Acronym	VMM-2					
Characteristic of your BTEX analyser						
Trademark	Synspec					
Model:	Syntech Spectras Analyser GC955					
Version:	GC955					
Year of manufacture:	2006					
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air	
Carrier gas:		X				
Other gases used:						
Operating system:	windows 98					
Cycle time, min:	15 min					
Adsorbent material:	tenax					
Sampling control	piston					
Sampling temperature, °C	27°C					
Sample volume, ml	140 ml					
Number of adsorbent tubes	1					
Desorption temperature, `	180°C					
Desorption time, sec	60 sec					
Desorption flow, ml/min	1,5 cc/min					
Cryo-trap detail						
Trapping temperature, °C						
Desorption temperature, °C		Desorption time, sec				
Desorption flow, ml/min		split flow, ml/min				
Stripper column	capillary column (2m)					
Analytical column	capillary column					
phase:	95% dimethylpolysiloxane + 5% diphenylpolysiloxane					
length, m:	13 m					
diameter (ID) mm:	0,32 mm					
thickness (µm):	1 µm					
analytical conditions:	50°C (3 min) --> 70°C (7 min) with a rate of 2°/min					
Traceability of your calibration Standard						
Certified reference material (CRM):						
Certified by						
Certified number:						
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)				
Benzene	11.33 ng/min	1.26 ng/min	k=3			
Toluene	10.64 ng/min	1.42 ng/min	k=3			
Ethyl-benzene	6.42 ng/min	1.12 ng/min	k=3			
m-Xylene	8.63 ng/min	1.43 ng/min	k=3			
p-Xylene	8.63 ng/min	1.43 ng/min	k=3			
o-Xylene	17.34 ng/min	2.13 ng/min	k=3			
Other methods						
Dilution of CRM						
Static Injection						
Permeation	portable permeation device, dilution possible between 600 and 1200 ml/min					
Additional comments						

VMM1 e 2

GRACE
Materials Technologies

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Sales Engineer
Grace Davison Discovery Sciences

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Frederik.Ottoy@Grace.com

Alltech Associates Inc
Brandstraat 12
9160 Lokeren, Belgium

Lokeren, 16 januari 2013
Ter attentie van Vincent Keppens, VMM Labo Gent

Betreft : offerte naar aanleiding van uw aanvraag
Onze referentie 20130116

Geachte,

Zoals afgesproken vindt u hierbij de door u aangevraagde offerte. Wij danken u voor de belangstelling die u in onze producten stelt.
Wij sturen u hierbij onze beste prijs voor de gevraagde producten :

Referentie	Aantal	Omschrijving	Prijs €
110-010-1400-F33-U40	1	Benzene,F33-StdEM Total Rate: 11ng/min ±50% at 40°C Accuracy: N/A Total Length: 4.5 cm ±10% Diameter: 0.64 cm	152.00
110-021-1401-F33-U40	1	Toluene,F33-StdEM Total Rate: 10ng/min ±50% at 40°C Accuracy: N/A Total Length: 5.6 cm ±10% Diameter: 0.64 cm	152.00
110-005-1405-T33-U40	1	Ethyl benzene,T33-Std#19 Total Rate: 12ng/min ±50% at 40°C Accuracy: N/A Total Length: 4 cm ±10% Diameter: 0.64 cm	152.00
110-005-1403-T33-U40	1	Xylene-m,T33-Std#19 Total Rate: 10ng/min ±50% at 40°C Accuracy: N/A Total Length: 4 cm ±10% Diameter: 0.64 cm	152.00
110-005-1404-T33-U40	1	Xylene-p,T33-Std#19 Total Rate: 18ng/min ±50% at 40°C Accuracy: N/A Total Length: 4 cm ±10% Diameter: 0.64 cm	152.00
110-007-1402-T33-U40	1	Xylene-o, T33-Std#19 Total Rate: 10ng/min ±50% at 40°C Accuracy: N/A Total Length: 4.2 cm ±10% Diameter: 0.64 cm	152.00
110-007-4206-F33-U40	1	1,2- dichloroethane, F33-StdEM Total Rate: 10ng/min ±50% at 40°C Accuracy: N/A Total Length: 4.2 cm ±10% Diameter: 0.64 cm	152.00

EKONERG

Participating Laboratory	EKONERG				
Acronym					
Characteristic of your BTEX analyser					
Trademark	Chromatorec				
Model:	Airmo BTX 1000				
Version:	GC FID				
Year of manufacture:	2011.				
	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:			X		
Other gases used:					X
Operating system:	Windows XP, Vistachrom				
Cycle time, min:	15				
Adsorbent material:	CarboTrap				
Sampling control	critical orifice 76um				
Sampling temperature, °C	40				
Sample volume, ml	480				
Number of adsorbent tubes	1				
Desorption temperature, `	380 C				
Desorption time, sec	120				
Desorption flow, ml/min					
Cryo-trap detail					
Trapping temperature, °C					
Desorption temperature, °C		Desorption time, sec			
Desorption flow, ml/min		split flow, ml/min			
Stripper column	MXT 30CE, film thickness: 1um, id: 0,28mm, length: 30m				
Analytical column					
phase:					
length, m:					
diameter (ID) mm:					
thickness (µm):					
analytical conditions:	init. temp. 60C, ramp 15C/min, end temp. 165C				
Traceability of your calibration Standard					
Certified reference material (CRM)	PRM - VSL				
Certified by	VSL				
Certified number:					
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)			
Benzene	12.00	0.36			
Toluene	11.96	0.36			
Ethyl-benzene	12.05	0.36			
m-Xylene	11.88	0.25			
p-Xylene	12.03	0.35			
o-Xylene	11.71	0.35			
Other methods					
Dilution of CRM					
Static Injection					
Permeation					
Additional comments					

EKONERG / Laboratorij za zrak
Zagreb, Koranska 5, tel. 01/6000-100

Naručitelj: DRŽAVNI HIDROMETEOROLOŠKI ZAVOD

Ugovor broj: I-02-611/13

CERTIFIKAT O UMJERAVANJU

br. 146/2013

Naziv instrumenta: AirmoBTX GC FID OS-1	Tvornička oznaka: 2841204
Umjeravanje obavljeno dana: 30.10.2012.	Mjerno područje: 0 – 50 ug/m^3
Umjerio: P. Hercog dipl. ing.	Izrada certifikata: P. Hercog dipl. ing.

Stanje instrumenta: Instrument je ispravan. Prije umjeravanja na instrumentu je napravljen godišnji servis sukladno uputama proizvođača.

Direktor odjela za mjerenja i analitiku:

Bojan Abramović, dipl. ing.

Direktor:

---

mr. sc. Zdravko Mužek, dipl. ing.

Zagreb, 23. studeni 2013.

Ovaj certifikat sastoji se od tri stranice i smije se prezentirati i kopirati jedino u cijelosti

1. METODA

Za umjeravanje koristili smo metodu M 05/LU opisanu u Radnoj uputi RULU/05-01. Instrument je umjeren upotrebom primarnog referentnog materijala.
Nakon umjeravanja na instrumentu su napravljeni testovi radnih karakteristika „lack of fit", ponovljivost i kratkotrajni pomak (drift) sukladno HRN EN 14662-3:2005

2. MJERNA SLJEDIVOST I OPREMA ZA UMJERAVANJE

Prilikom umjeravanja osigurana je mjerna sljedivost primarnog referentnog materijala (VSL PRM cylinder no. 9306834) pomoću certifikata sljedivog do SI standarda. Mjerna sljedivost i oprema dani su u tablici 1.
Dokazi o sljedivosti opreme nalaze se u Prilogu 1.

Tablica 1

Oprema	Funkcija opreme	Sljedivost
VSL PRM boca sa BTX u N_2	Primarni referentni materijal	Cerifikat br. 3221969.01
Boca sa benzen u N_2 34,77 mg/m^3	Certificirani referentni materijal	Cerifikat br. UP 01/13 izdan u Ekonerg laboratoriju za zrak
Kalibrator Horiba	Referentna dilucijska jedinica	Certifikati o umjeravanju br. 6013-KL-M0029-13 6013-KL-M0030-13 izdani u akreditiranom laboratoriju ČMI Brno
Sustav za generiranje nul zraka	Izvor nul zraka	Odobren u našem laboratoriju neposredno prije umjeravanja pomoću referentnog instrumenta

3. MJERNA NESIGURNOST UMJERAVANJA

Izražena proširena mjerna nesigurnost umjeravanja označena je kao sastavljena mjerna nesigurnost pomnožena sa obuhvatnim faktorom k=2 što u slučaju normalne distribucije daje približno 95% pokrivenosti. Standardne mjerne nesigurnosti kao sastavnice sastavljene mjerne nesigurnosti određene su u skladu sa EA-4/02 i HRN EN 14662:2005 dio III.

3.1 Sastavnice sastavljene mjerne nesigurnosti

- standardna mjerna nesigurnost zbog kalibracijskog plina

3.2 Mjerna nesigurnost umjeravanja

Tablica 2.

Plin	Koncentracija plina (ppb)	Proširena mjerna nesigurnost Uxi (ppb)
Benzen	12,00	0,36
Toluen	11,96	0,36
Etilbenzen	12,05	0,36
p-ksilen	12,03	0,36
m-ksilen	11,88	0,35
o-ksilen	11,71	0,35

EKONERG

4. REZULTATI UMJERAVANJA

Originalni podatci nalaze se u laboratorijskom računalu na C:\Documents and Settings\phercog\My Documents\Laboratorij\Kalibracije 2013\BTX

4.1 Laboratorijski uvjeti

Temperatura zraka: 21+/- 1,5 °C
Relativna vlažnost zraka: 37-42 %

4.2 Važni parametri uzorkovanog plina

Temperatura: 21+/- 1,5 °C

4.3 Postavljeni faktori

Bazna osjetljivost: 6037,99

4.4 Rezultati testova radnih karakteristika

Instrument je zadovoljio granice prihvatljivosti definirane HRN EN 14662-3:2005. Rezultati su prikazani u Tablici 3.

Tablica 3

Tablica ocjene testova radnih karakteristika					
Br. testa iz Tablice 2 iz EN 14662-3	Oznaka iz EN 14662-3	Naziv testa	Rezultat testa	Granice prihvatljivosti	Ocjena
3	r_{LV}	ponovljivost na graničnoj vrijednosti za god. GV	1,03%	< 5,0 %	zadovoljava
2	$r_{0,5}$	ponovljivost na 1/10 GV	0,08	< 0,3 ug/m^3	zadovoljava
1	X_I	lack of fit test za točke različite od 0	2,34%	< 5% mjerene vr. u bilo kojoj točki	zadovoljava
formula (33)	L	granica detekcije	0,08	N/A	N/A
10	d_{24}	kratkotrajni odmak na span plinu	0,01%	< 5,0 %	zadovoljava

4.5 Rezultati odziva instrumenta na referentni plin

Tablica 4

Generirana koncentracija plina (ug/m^3)	Koncentracija plina mjerena umjerenim instrumentom (ug/m^3)
0,00	0,00
8,16	8,12
24,02	24,79
32,85	33,94
42,58	44,24

HMS

Participating Laboratory	Air Quality Reference Center, Hungarian Meteorological Service
Acronym	AQRC-HMS (LRK-OMSZ)

Characteristic of your BTEX analyser

Trademark	CHROMATOTEC/AIRMOTEC
Model:	airmoVOC C6-C12
Version:	A31000
Year of manufacture:	2003

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:			X		
Other gases used:					X

Operating system:	Windows XP		
Cycle time, min:	30 min		
Adsorbent material:	MXT 30 CE		
Sampling control	pump		
Sampling temperature, °C	36		
Sample volume, ml	~ 415 ml		
Number of adsorbent tubes	3		
Desorption temperature, `	380		
Desorption time, sec	240		
Desorption flow, ml/min	3		
Cryo-trap detail	-		
Trapping temperature, °C	-		
Desorption temperature, °C	-	Desorption time, sec	-
Desorption flow, ml/min	-	split flow, ml/min	-
Stripper column	-		
Analytical column	MXT 30 CE		
phase:			
length, m:	30		
diameter (ID) mm:	0.28		
analytical conditions:	°C (duration 360 s), gradiant 10°C/min to 80°C (duration 180 s), gradiant 15°C/m		

Traceability of your calibration Standard

Certified reference material (CRM):	VSL Dutch Metrology Institute	
Certified by	VSL Dutch Metrology Institute	
Certified number:	3221915	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ppb (mol/mol)
Benzene	986 x 10^{-9}	29 x 10^{-9}
Toluene	985 x 10^{-9}	29 x 10^{-9}
Ethyl-benzene	995 x 10^{-9}	30 x 10^{-9}
m-Xylene	983x 10^{-9}	29 x 10^{-9}
p-Xylene	982 x 10^{-9}	29 x 10^{-9}
o-Xylene	1014 x 10^{-9}	30 x 10^{-9}

Other methods	
Dilution of CRM	dilution range: 2-9 ppb by Environics 200 diluitor
Static Injection	-
Permeation	-
Additional comments	

HMS

száma: s50.1/2013

Országos Meteorológiai Szolgálat
Éghajlati és Levegőkörnyezeti Főosztály
LRK – Kalibráló Laboratórium
Központ: 1024 Budapest, Kitaibel Pál u. 1.
Telephely: 1113 Budapest, Aga u. 4.
Telefon: 209 1000
Telefax: 209 5759

A NAT által NAT-2-0285/2009 számon akkreditált kalibráló laboratórium

KALIBRÁLÁSI BIZONYÍTVÁNY

száma: s50.1/2013

Mérőeszköz megnevezése:	BTEX (C6-C12) gázelemző
Típusa:	A31000
Gyártó:	Airmotec
Gyári száma:	2020100
A megrendelő neve:	OMSZ ÉLFO LRK Kalibráló Laboratórium
Kalibrálás helye:	OMSZ ÉLFO LRK Kalibráló Laboratórium
Kalibrálás ideje:	2013.10.21-22.
Kalibrálás módszere:	Minőségirányítási Kézikönyvben rögzített "B1" módszer - (gázkeverő berendezés alkalmazásával, tanúsított anyagminta felhasználásával)
Kalibrálás körülményei:	környezeti hőmérséklet: 22,5 °C
	légköri nyomás: 1004 hPa

Kalibrálást végezte: Pólay Gábor

HMS

Országos Meteorológiai Szolgálat
Éghajlati és Levegőkörnyezeti Főosztály
LRK – Kalibráló Laboratórium

A NAT által NAT-2-0285/2009 számon akkreditált kalibráló laboratórium

A kalibrálásnál alkalmazott tanúsított anyagminták és kalibráló berendezések visszavezetettsége hitelesítéssel, illetve kalibrálással biztosított:

Gázkeverő készülék: típ.: Environics S-200, gy.sz.: 1823, Kal. biz. sz.: s03/2013;
VOC/N_2 1 ppm ± 0,05 ppm (n/n), VSL palack sz: 930734, Kal.biz sz.: 3221915;
Digitális hőmérő: típ.: Almemo 2290-3, gy.sz.: 942911, Kal. biz. sz.: Hőm-0260/2013;
Légnyomásmérő: típ.: Almemo 2290-2/3, gy.sz.: 942911, Kal. biz. sz.: KAL-036/2013;
Segédanyag: '0'-levegő, nullgáz generátorral előállítva.

Mérési eredmények:

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,000	ppb	-
2,958	ppb	**Benzol**/N_2:0-lev	2,968	ppb	0,13 ppb
5,916	ppb	"	6,027	ppb	0,27 ppb
8,874	ppb	"	8,912	ppb	0,40 ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,00	ppb	-
2,949	ppb	**n-Heptán**/N_2:0-lev	2,694	ppb	0,13 ppb
5,898	ppb	"	5,489	ppb	0,27 ppb
8,847	ppb	"	8,054	ppb	0,40 ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,012	ppb	-
2,955	ppb	**Toluol**/N_2:0-lev	2,971	ppb	0,13 ppb
5,910	ppb	"	6,120	ppb	0,27 ppb
8,865	ppb	"	8,922	ppb	0,40 ppb

Kalibrálást végezte: Pólay Gábor

HMS

Országos Meteorológiai Szolgálat
Éghajlati és Levegőkörnyezeti Főosztály
LRK – Kalibráló Laboratórium

A NAT által NAT-2-0285/2009 számon akkreditált kalibráló laboratórium

Mérési eredmények (folytatás):

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)	Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,000 ppb	-
3,000	ppb	**n-Oktán**/N_2:0-lev	2,815 ppb	0,14 ppb
6,000	ppb	"	5,844 ppb	0,27 ppb
9,000	ppb	"	8,593 ppb	0,41 ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)	Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,014 ppb	-
2,985	ppb	**Etilbenzol**/N_2:0-lev	2,994 ppb	0,14 ppb
5,970	ppb	"	6,184 ppb	0,27 ppb
8,955	ppb	"	9,011 ppb	0,41 ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)	Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,024 ppb	-
2,949	ppb	**m-Xilol**/N_2:0-lev	3,049 ppb	0,13 ppb
5,898	ppb	"	6,387 ppb	0,27 ppb
8,847	ppb	"	9,422 ppb	0,40 ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)	Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,024 ppb	-
2,946	ppb	**p-Xilol**/N_2:0-lev	3,049 ppb	0,13 ppb
5,892	ppb	"	6,387 ppb	0,27 ppb
8,838	ppb	"	9,422 ppb	0,40 ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)	Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,020 ppb	-
3,042	ppb	**o-Xilol**/N_2:0-lev	3,060 ppb	0,14 ppb
6,084	ppb	"	6,354 ppb	0,28 ppb
9,126	ppb	"	9,610 ppb	0,41 ppb

Kalibrálást végezte: Pólay Gábor

HMS

Országos Meteorológiai Szolgálat
Éghajlati és Levegőkörnyezeti Főosztály
LRK – Kalibráló Laboratórium

A NAT által NAT-2-0285/2009 számon akkreditált kalibráló laboratórium

Mérési eredmények (folytatás):

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)	Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,023 ppb	-
2,988	ppb	**135-TMB** /N_2:0-lev	2,657 ppb	0,18 ppb
5,976	ppb	"	6,051 ppb	0,36 ppb
8,958	ppb	"	8,658 ppb	0,55 ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)	Mérési bizonytalanság (U)*
0,000	ppb	'0'-levegő	0,030 ppb	-
3,021	ppb	**124-TMB** /N_2:0-lev	2,553 ppb	0,18 ppb
6,042	ppb	"	5,976 ppb	0,37 ppb
9,063	ppb	"	8,385 ppb	0,55 ppb

* A kalibrálás U kiterjesztett bizonytalansága az EA-4/02 dokumentumnak megfelelően az u(y) eredő bizonytalanságnak a k = 2 kiterjesztési tényezővel szorzott értéke, ami normális eloszlás esetén közelítőleg 95% fedési valószínűségnek felel meg.

Megjegyzés:

- A kalibrálás eredménye a talált metrológiai jellemzőket rögzíti.
- Kalibrálás alatt a készülék az alábbi beállításokkal rendelkezett:

Mérési program:	AMB-30MN
Retenciós tábla:	VOC#202
Minta térfogata (Sample volume):	418,9 ml
FID hőm.:	170,0 °C
Érzékenység (Base sensitivity):	5308,0
Detektor jel erősítés (Amplification level)	3-High

Kiállítás kelte: Budapest, 2013.10.31.

Kiadható:

Kalibrálást végezte: Pólay Gábor

Dézsi Viktor
osztályvezető

Készült 1 példányban. A jelen bizonyítvány csak teljes formájában és terjedelmében érvényes és másolható.

EPA1

Participating Laboratory	Enviromental protection Agency Ireland				
Acronym	EPA				
Characteristic of your BTEX analyser					
Trademark	Syntech				
Model:	GC955				
Version:	600				
Year of manufacture:	2008				
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		yes			
Other gases used:					
Operating system:	Windows XP				
Cycle time, min:	15 min				
Adsorbent material:	Tenax GR 35/60				
Sampling control	sample pump/piston pump				
Sampling temperature, °C	30				
Sample volume, ml	210				
Number of adsorbent tubes	1				
Desorption temperature, `	180				
Desorption time, sec	60				
Desorption flow, ml/min	1.5				
Cryo-trap detail	n/a				
Trapping temperature, °C					
Desorption temperature, °C		Desorption time, sec			
Desorption flow, ml/min		split flow, ml/min			
Stripper column	2m				
Analytical column	CP-Sil 8 CB				
phase:	100% dimethylpolysiloxane phase				
length, m:	13				
diameter (ID) mm:	0.32				
thickness (µm):	1.0				
analytical conditions:	50C for 3mins, ramp @ 10C/min to 70C, hold for 7mins, ramp @ 10C/min to 50C and hold.				
Traceability of your calibration Standard					
Certified reference material (CRM):	NPL				
Certified by	NPL				
Certified number:	2013060090				
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)			
Benzene	10.14	0.2			
Toluene	10.27	0.26			
Ethyl-benzene	9.69	0.24			
m-Xylene	10.18	0.25			
p-Xylene	9.8	0.25			
o-Xylene	10.25	0.26			
Other methods					
Dilution of CRM					
Static Injection					
Permeation					
Additional comments					

EPA2

Participating Laboratory	Enviromental protection Agency Ireland
Acronym	EPA
Person(s) responsible	Lin Delaney

Characteristic of your BTEX analyser

Trademark	Syntech
Model:	GC955
Version:	611
Year of manufacture:	2010

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		yes			
Other gases used:					

Operating system:	Windows XP		
Cycle time, min:	15 min		
Adsorbent material:	Tenax GR 35/60		
Sampling control	sample pump/piston pump		
Sampling temperature, °C	30		
Sample volume, ml	210		
Number of adsorbent tubes	1		
Desorption temperature, `	180		
Desorption time, sec	60		
Desorption flow, ml/min	1.5		
Cryo-trap detail	n/a		
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column			2
Analytical column	CP-Sil 8 CB		
phase:	100% dimethylpolysiloxane phase		
length, m:	28		
diameter (ID) mm:	0.32		
thickness (µm):	1.0		
analytical conditions:	50C for 3mins, ramp @ 10C/min to 70C, hold for 7mins, ramp @ 10C/min to 50C and hold.		

Traceability of your calibration Standard

Certified reference material (CRM):	NPL	
Certified by	NPL	
Certified number:	2013060090	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	10.14	0.2
Toluene	10.27	0.26
Ethyl-benzene	9.69	0.24
m-Xylene	10.18	0.25
p-Xylene	9.8	0.25
o-Xylene	10.25	0.26

Other methods	
Dilution of CRM	
Static Injection	
Permeation	
Additional comments	

EPA 1 e 2

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

4002

PRIMARY REFERENCE GAS MIXTURE

Cylinder Number: D03 5741

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: **Environmental Protection Agency**

ADDRESS: National Ambient Air Quality Programme, Seville Lodge, Callan Road, Kilkenny, Ireland

CALIBRATION DATE: 23 September 2013

AMOUNT FRACTIONS:

Component	Amount Fraction / (nmol/mol)
Benzene	10.14 ± 0.20
Toluene	10.27 ± 0.26
Ethylbenzene	9.69 ± 0.24
m-xylene	10.18 ± 0.25
p-xylene	9.80 ± 0.25
o-xylene	10.25 ± 0.26
Nitrogen	balance

The reported uncertainties of the results are based on standard uncertainties multiplied by a coverage factor of $k = 2$, providing a level of confidence of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; minimum utilisation pressure: 10 bar

STORAGE: No special requirements

HANDLING: Refer to ISO 16664

OUTLET: DIN477 No.1 valve

INTENDED USE: Calibration standard

Reference: 2013060090 **Date of issue:** 26 September 2013

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

Page 1 of 1

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

AAA

Participating Laboratory	Environmental Protection Agency (Lithuania)
Acronym	EPA AAA

Characteristic of your BTEX analyser

Trademark	AMA Instruments
Model:	GC 5000 BTX FID
Version:	3
Year of manufacture:	2011

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		X			
Other gases used:			X		X

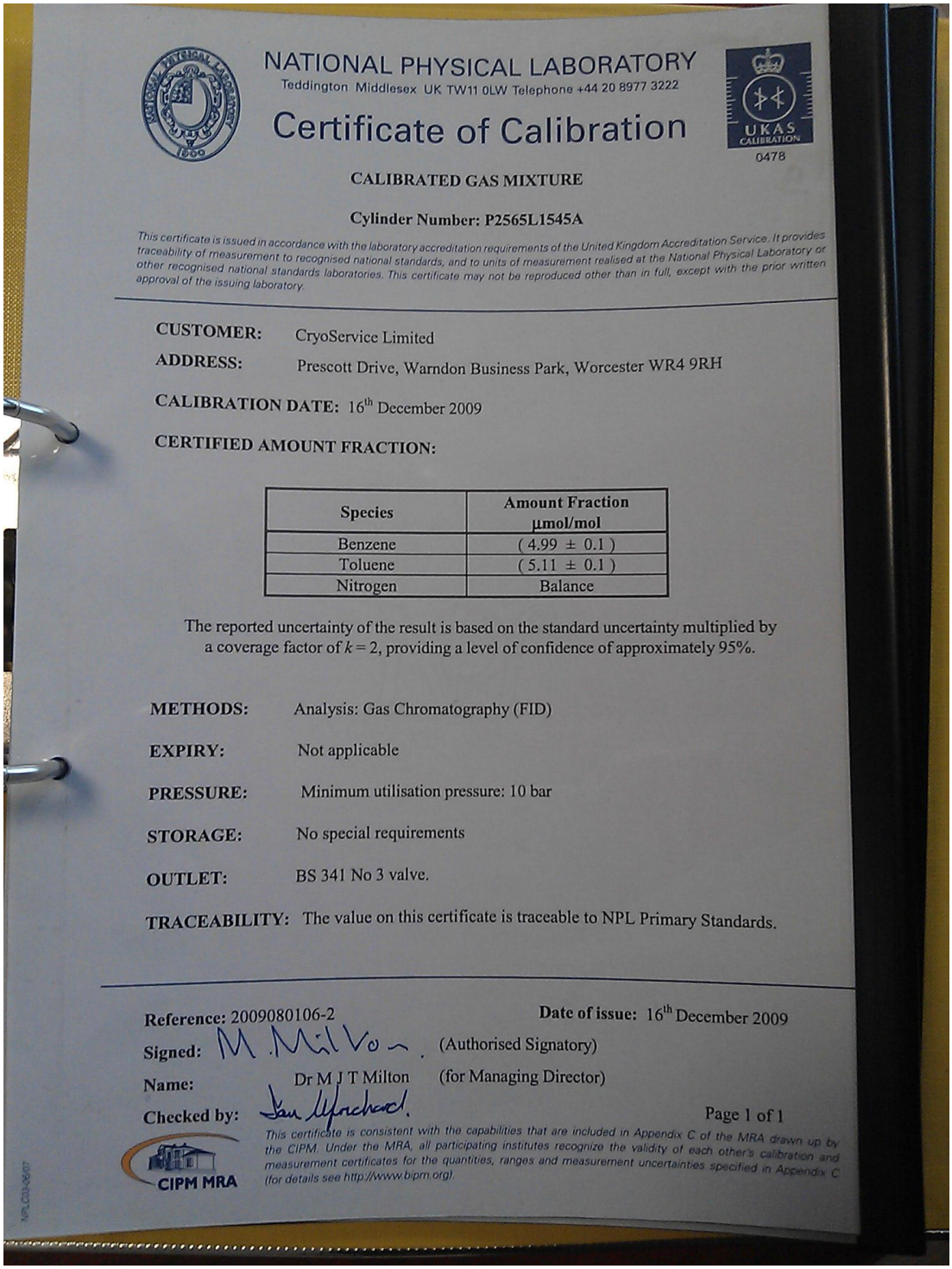
Operating system:	Windows XP Professional		
Cycle time, min:	30		
Adsorbent material:	Carbotrap		
Sampling control	MFC		
Sampling temperature, °C	30		
Sample volume, ml	300		
Number of adsorbent tubes	1		
Desorption temperature,	230 °C		
Desorption time, sec	180		
Desorption flow, ml/min	2		
Cryo-trap detail	none		
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	none		
Analytical column			
phase:	AMAsep 1		
length, m:	30		
diameter (ID) mm:	0.32		
thickness (µm):	1.5		
analytical conditions:	50°C (3min), 8°C/min, 130°C (5min)		

Traceability of your calibration Standard

Certified reference material (CRM):	Calibrated Gas Mixture	
Certified by	National Physical Laboratory (UK)	
Certified number:	-	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	4990	100
Toluene	5110	100
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		

Other methods	
Dilution of CRM	dilution factor: 500, Dilutor: Umwelttechnik MCZ GmbH
Static Injection	
Permeation	Benzene 15ng/min, temperature: 50°C, Horiba GmbH
Additional comments	

AAA



NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS CALIBRATION 0478

CALIBRATED GAS MIXTURE

Cylinder Number: P2565L1545A

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: CryoService Limited

ADDRESS: Prescott Drive, Warndon Business Park, Worcester WR4 9RH

CALIBRATION DATE: 16th December 2009

CERTIFIED AMOUNT FRACTION:

Species	Amount Fraction µmol/mol
Benzene	(4.99 ± 0.1)
Toluene	(5.11 ± 0.1)
Nitrogen	Balance

The reported uncertainty of the result is based on the standard uncertainty multiplied by a coverage factor of $k = 2$, providing a level of confidence of approximately 95%.

METHODS: Analysis: Gas Chromatography (FID)

EXPIRY: Not applicable

PRESSURE: Minimum utilisation pressure: 10 bar

STORAGE: No special requirements

OUTLET: BS 341 No 3 valve.

TRACEABILITY: The value on this certificate is traceable to NPL Primary Standards.

Reference: 2009080106-2 **Date of issue:** 16th December 2009

Signed: M. Milton (Authorised Signatory)

Name: Dr M J T Milton (for Managing Director)

Checked by: Ian Uprichard

Page 1 of 1

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

GIOS

Participating Laboratory	Chief Inspectorate of Environmental Protection
Acronym	GIOS

Characteristic of your BTEX analyser

Trademark	Syntech Spectras				
Model:	GC955				
Version:	601				
Year of manufacture:	2011				
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		X			
Other gases used:					
Operating system:	Windows xp				
Cycle time, min:	15				
Adsorbent material:	Tenax				
Sampling control	piston				
Sampling temperature, °C	ambient				
Sample volume, ml	35				
Number of adsorbent tubes	1				
Desorption temperature, `	180				
Desorption time, sec	26				
Desorption flow, ml/min	1.5				
Cryo-trap detail					
Trapping temperature, °C					
Desorption temperature, °C		Desorption time, sec			
Desorption flow, ml/min		split flow, ml/min			
Stripper column	SY-5 15m, 0.32 mm ID, 1 µm film, 2m,				
Analytical column	Synspec				
phase:					
length, m:	13				
diameter (ID) mm:	0.32				
thickness (µm):	1				
analytical conditions:	50°C (1-3min), 10°C/min, 70°C (5-12min), -8°C/min, 50°C(13,5-15min)				

Traceability of your calibration Standard

Certified reference material (CRM):	Air Liquide Polska	
Certified by	Air Liquide Deutschland GmbH	
Certified number:	9382636001	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	1170	59
Toluene	855	85.5
Ethyl-benzene	815	81.5
m-Xylene	714	71.4
p-Xylene	695	69.5
o-Xylene	650	65
Other methods		
Dilution of CRM	CGM2000, 10ppb	
Static Injection		
Permeation		
Additional comments		

GIOS

AIR LIQUIDE

TEST REPORT

AIR LIQUIDE Deutschland GmbH
Bataverstrasse 47
47809 KREFELD

ORDER DATA

Determination of C_6H_6, C_8H_{10}, C_7H_8, C_9H_{12}, C_8H_{10} and C_8H_{10} in AIR	Order-/GLB-No. : 27355397-10
Customer : AIR LIQUIDE POLSKA SP ZOO Payable Accounting - Interco Al.Pilsudskiego 92 41-308 DABROWA GORNICZA	Date of receipt: 10.09.2013

TEST

[X] Test Report acc. to DIN EN ISO/IEC 17025	[ ] Amendment / Addition	[ ] Correction

Test item:
1 Aluminium gas cylinder (10 L), Cylinder No. : D3CE061

Test Parameter(s) Determination of			Test Method:
BENZENE	1,10	Mol-ppm	GAS-CHROMATOGRAPHY-FID
ETHYL BENZENE	1	Mol-ppm	GAS-CHROMATOGRAPHY-FID
TOLUENE	1	Mol-ppm	GAS-CHROMATOGRAPHY-FID
M-XYLENE	1	Mol-ppm	GAS-CHROMATOGRAPHY-FID
O-XYLENE	1	Mol-ppm	GAS-CHROMATOGRAPHY-FID
P-XYLENE	1	Mol-ppm	GAS-CHROMATOGRAPHY-FID

SAMPLING
Gas Withdrawal by Pressure Reducer / Needle Valve

ATTACHMENTS
Air Liquide Certificate of Analysis

Durch die DAkkS Deutsche Akkreditierungsstelle GmbH
akkreditiertes Prüflaboratorium
Die Akkreditierung gilt für die in der Urkunde
aufgeführten Prüfverfahren

DAkkS Deutsche Akkreditierungsstelle D-PL-14641-01-00

AIR LIQUIDE

TEST REPORT

AIR LIQUIDE Deutschland GmbH
Bataverstrasse 47
47809 KREFELD

SUMMARY OF RESULTS[1]

Analyse	Content		MU % rel
BENZENE	1,117	Mol-ppm	5
ETHYL BENZENE	0,815	Mol-ppm	10
TOLUENE	0,855	Mol-ppm	10
M-XYLENE	0,714	Mol-ppm	10
O-XYLENE	0,650	Mol-ppm	10
P-XYLENE	0,695	Mol-ppm	10

TEXT

Air Liquide 's Primary Internal Standards, used for the calibration of the measuring equipment mentioned above, are high precision gravimetric gas mixtures, manufactured by Air Liquide according to ISO 6142 and are traceable to SI mass units.

Uncertainty: ± 2 σ (coverage factor K = 2)
MU = Uncertainty of measurement

Date of Test 10.10.2013

Axel Ortmanns
Prüf- und Kalibrierlabor
Laborleiter
Tel.: 02151/954-145

---------- END OF TEST REPORT ----------

[1] The test results relate only to the items tested.

Durch die DAkkS Deutsche Akkreditierungsstelle GmbH
akkreditiertes Prüflaboratorium
Die Akkreditierung gilt für die in der Urkunde
aufgeführten Prüfverfahren

DAkkS Deutsche Akkreditierungsstelle D-PL-14541-01-00

IPH_S

Participating Laboratory	Institute of Public Health of Belgrade
Acronym	IPH

Characteristic of your BTEX analyser

Trademark	SYNTECH SPECTRAS
Model:	GC 955
Version:	601
Year of manufacture:	2009

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		X			
Other gases used:					

Operating system:	Windows XP		
Cycle time, min:	15 min		
Adsorbent material:	Tenax GR		
Sampling control	piston pump + MFC		
Sampling temperature, °C	Ambient		
Sample volume, ml	210		
Number of adsorbent tubes	one		
Desorption temperature, `	180 C		
Desorption time, sec	60		
Desorption flow, ml/min	1.5		
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	identical with analytical column, 2m lenght		
Analytical column	AT624		
phase:	(6% Cyanopropylphenyl)-94% methylpolysiloxane		
length, m:	15		
diameter (ID) mm:	0.32		
thickness (µm):	1		
analytical conditions:	50 C (3 min),50-70 C ,10C/min, 70C (5-12 min), 70-50 C ,10C/min, 50C (14-15 min)		

Traceability of your calibration Standard

Certified reference material (CRM):		
Certified by		
Certified number:		
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene		
Toluene		
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		
Other methods		
Dilution of CRM	e (MFCs+cylinder), is calibrated in calibration laboratoray in Czech Hydromete	
Static Injection		
Permeation		
Additional comments		

Certified of calibration not provided by the laboratory

IPH_S

ISCIII

Participating Laboratory	INSTITUTO DE SALUD CARLOS III
Acronym	ISCIII

Characteristic of your BTEX analyser

Trademark	SYNTECH SPECTRAS
Model:	GC955
Version:	
Year of manufacture:	2004

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		X			
Other gases used:					

Operating system:	WINDOWS			
Cycle time, min:	15 min			
Adsorbent material:	Tenax GR 60-80			
pump	pump/MFC/piston			
Sampling temperature, °C	≈ 25 °C			
Sample volume, ml	50 ml			
Number of adsorbent tubes	--			
Desorption temperature, `	5 °C - 35 °C			
Desorption time, sec				
Desorption flow, ml/min				
Cryo-trap detail	--			
Trapping temperature, °C				
Desorption temperature, °C	180 °C	Desorption time, sec	40 s	
Desorption flow, ml/min	1,5 ml/min	split flow, ml/min		
Stripper column	dimetil-polixiloxano (94 %) and ciano-propil-fenilo (6 %); 2 m			
Analytical column	AT-624			
phase:	dimetil-polixiloxano (94 %) and ciano-propil-fenilo (6 %)			
length, m:	13 m			
diameter (ID) mm:	0,32 mm			
thickness (µm):	1,8 µm			
analytical conditions:	50°C (3'),10°C/min,70°C (6'), 10°C/min 50°C			

Traceability of your calibration Standard

Certified reference material (CRM):	VSL	
Certified by	VSL	
Certified number:		
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	149.9	4.5
Toluene	149.3	4.5
Ethyl-benzene	150.5	4.5
m-Xylene	148.1	4.5
p-Xylene	150.3	4.5
o-Xylene	146.2	4.4

Other methods	
Dilution of CRM	API 700
Static Injection	
Permeation	

Additional comments

Data of our calibration standard are aproximate. Maybe we will have to acquire a new calibtration standard before the intercomparison

VSL
Dutch Metrology Institute

2A UC-18

CERTIFICATE

Number 3222029
Page 1 of 1

Reference material of BTEX

Description: Primary reference gas mixture (PRM), cylinder number 930732.
The cylinder contains a mixture of BTEX in nitrogen.
The PRM is contained in a passivated aluminium cylinder. The cylinder has a water volume of 5 L and is pressurized to 11.9 MPa.
Cylinder outlet conforms to DIN 1 specifications.

Method of preparation: Gravimetric preparation in accordance with ISO 6142: 2001 (Gas analysis - Preparation of calibration gas mixtures - Gravimetric method).

Result

Amount fraction	Concentration [mol/mol]	Uncertainty [mol/mol]
benzene	149.9×10^{-9}	4.5×10^{-9}
toluene	149.3×10^{-9}	4.5×10^{-9}
o-xylene	146.2×10^{-9}	4.4×10^{-9}
ethylbenzene	150.5×10^{-9}	4.5×10^{-9}
m-xylene	148.1×10^{-9}	4.4×10^{-9}
p-xylene	150.3×10^{-9}	4.5×10^{-9}

The reported uncertainty of measurement is based on the standard uncertainty multiplied by a coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard uncertainty has been determined in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM).

Traceability: The values on this certificate are traceable to VSL Primary Standards.

Safety information: The cylinder should be handled with care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of gaseous materials.

Instructions for use: The material can be used to validate and/or calibrate analytical methods applied.

Do not use the cylinder in case the cylinder pressure is below 1 MPa.
More instructions can be found in ISO 16664:2004 (Gas analysis – Handling of calibration gases and gas mixtures – Guidelines).

Expiry date: The certificate is valid until 9 August 2015.

Delft, 22 August 2012
VSL B.V.

J.I.T. van Wijk
Allround metrologist

VSL
Dutch

Participating Laboratory	Ricardo-AEA
Acronym	R-AEA

AEA

Characteristic of your BTEX analyser

Trademark	Environnement
Model:	Clarus 5000 VOC71M
Version:	
Year of manufacture:	2004

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		Y			
Other gases used:					

Operating system:			
	Windows		
Cycle time, min:	15 or 30 minutes		
Adsorbent material:	carbotrap/Carbopack X mixture		
Sampling control	Internal trap with critical orifice		
Sampling temperature, °C	Ambient		
Sample volume, ml	1050/2100		
Number of adsorbent tubes	2		
Desorption temperature, `	350		
Desorption time, sec	180		
Desorption flow, ml/min	1		
Cryo-trap detail	CarboPack X		
Trapping temperature, °C	32		
Desorption temperature, °C	350	Desorption time, sec	3
Desorption flow, ml/min	1	split flow, ml/min	
Stripper column			
Analytical column	Supalco SPB 624		
phase:	Proprietry, bonded		
length, m:	13		
diameter (ID) mm:	0.32		
thickness (µm):	1.8		
analytical conditions:	34° for 115 seconds, ramp of 20 C/min for 260 sec, 150° for 155 seconds		

Traceability of your calibration Standard

Certified reference material (CRM):		
Certified by	NPL	
Certified number:		
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	3.76	0.08
Toluene	3.78	0.08
Ethyl-benzene	3.81	0.08
m-Xylene	3.78	0.08
p-Xylene	3.8	0.08
o-Xylene	3.8	0.08
Other methods		
Dilution of CRM		
Static Injection		
Permeation		
Additional comments		

ertified of

Certified of calibration not provided by the laboratory

AEA

European Commission
EUR 27012 EN – Joint Research Centre – Institute for Environment and Sustainability

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Stimulating innovation
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